Abstract

Activated alumina and zinc oxide both have been used as a sulphur remover catalyst in different applications such as gas, oil and petrochemicals. One of the main applications of activated alumina is removing of sulphur from sour natural gas in Claus process and also ZnO can be used as a catalyst agent or support performing a Fischer Tropsch reaction to convert a mixture of carbon monoxide and hydrogen to hydrocarbons [1]. Apart from gas, oil and petrochemical processing, removing of the sulphur to have clean environment also is very important. In this study we have tried to investigate synthesis of alumina and zinc oxide when they prepare in chemical root at the same time. Precipitation of alumina and zinc oxide was performed by mixing of aluminum chloride and zinc acetate in different proportions. Calcined materials were characterized by DSC, XRD, BET, SEM and FTRI to see phase distribution and its effect on surface area activation. Also dispersion of different proportions of Al₂O₃-ZnO to have maximum surface area was evaluated.

Keywords
Phase distribution, co-precipitation, Sulphur, catalyst, Al₂O₃-ZnO.

1 Introduction

Alumina and zinc oxide investigated in various methods in recent years and different applications are defined for these materials such as, catalyst, electronic devices, IR absorber, pigment components, medical and cosmetic. In all of these applications control of particle size, particles distribution and component morphology have been special attention since the effect of these parameters in final properties are very important [2]. Also these materials can be used as a catalyst support for verifications of microstructure and morphology of final
components. Therefore these materials have been used in heterogeneous catalyst in recent years. Heterogeneous catalytic oxidation has been demonstrated as an efficient abatement technology for the removal of sulphur constitutions [2]. The activity and performance of catalyst are influenced by their chemical compositions and preparation methods. One of the main applications of these materials is as sulphur remover catalysts which both alumina and zinc oxide have been used in oil, gas and petrochemical industries.

The removal of sulphur-containing species is currently a strategic issue [3]. Hydrogen sulphide gas occurs naturally in crude petroleum, natural gas, volcanic gases and hot springs. It also can result from industrial activities, such as food processing, coke ovens, kraft paper mills, tanneries and petroleum refineries. Many industrial processes, such as the Claus process and natural gas sweetening, are characterized by H$_2$S streams at relatively low temperatures [4].

The natural gas composed of light hydrocarbons in which methane is the major one. As far as the sulphur compounds are concerned hydrogen sulfide is the important one with carbonyl sulfide, carbon disulfide and mercaptans. Zinc oxide is the most important materials that can be used to remove the traces amount hydrogen sulfide being present in the gas mixture. The natural gas or naphtha feed were heated to 285-400 °C and then passed through one or more bed of ZnO in the form of tablets, spheres, or extrudates where the function of the catalyst depends on the chemical reaction [5]:

\[
\text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O}
\]

Usually zinc oxide catalyst is used as a mixture of ZnO and alumina as a binder, in general 90 \%wt of ZnO is quiet acceptable. Catalysts deactivation are governed by several factors and the three most important are poisoning, fouling and sintering of the catalysts [6]. Regenerability of ZnO discussed by Susan is restricted by loss of surface area at high regeneration temperatures and formation of zinc sulfate at low regeneration temperatures. Also, during sulfidation, reduction of ZnO followed by vaporization of elemental zinc can take place at temperatures below 600 °C [7].

Among adsorbents for H$_2$S removal at low temperature, zinc oxide (ZnO) has a very high equilibrium constant, removing H$_2$S down to fractions of 1 ppm [8]. Therefore, ZnO nanoparticle was chosen as the active species. In this research phase distribution of co-precipitated alumina and zinc components were synthesized in order to get maximum surface area. The behavior of zinc anion salt on base aluminium cautions to form ZnO nano catalyst demonstrated. Also special methods for de-agglomeration of zinc oxide to have suitable surface area and control in uniform morphology were established. Since the penetration of hydrogen sulphide in matrix is a slow process, it needs locations to increase the absorption of sulphur components. Therefore a matrix based on alumina with high surface area can be modulating to have maximum absorption of sulphur components by zinc oxide. To increase reaction between H$_2$S containing gases and ZnO, a matrix of meso and macro porous with high surface area is needed. Therefore incorporation of ZnO in porous alumina can perform this idea.

Therefore the aim of the present investigation is to establish a new practical method to activate the ZnO catalyst by incorporating porous alumina.
The characterizations of materials during experiments were carried out by DSC, BET, XRD and FTIR analysis to obtain more information in the development of new adsorbents. The results have shown that the as-synthesized materials have conspicuous performance for high surface area ZnO-Al$_2$O$_3$ composite.

2 Materials and methods

The raw materials with high purity included aluminium chloride (AlCl$_3$) and zinc acetate (Zn(O$_2$CCH$_3$)$_2$(H$_2$O)$_2$) were selected. Different samples were prepared by mixing of raw materials in a procedure that explained in follow and the proportions of them are shown in Table 1.

For AZ1, 80 grams of aluminium chloride was dissolved in 100 ml of de-ionized water at temperature of 60°C while stirring and then 90 ml of ammonia was slowly added to precipitate white porous and puffy of aluminium chloride. The solid product was filtered, washed and dried in oven at temperature of 90°C. For AZ2 to AZ5 same procedures were used as AZ1 with addition of zinc acetate. In AZ2 30 grams of zinc acetate was dissolved in 20 ml of de-ionized water at temperature of 60°C while stirring, at the same time 60 grams of aluminium chloride was dissolved in 90 ml of de-ionized water, then two solutions were mixed together. To precipitate the composition of these two mixture 80 ml of ammonia was slowly added to the mixture to have PH of 12. Precipitated white gel of aluminium chloride and zinc acetate solid was filtered, washed and dried in oven at temperature of 90°C. To obtain best calcination temperature DSC analysis was carried out on three samples of AZ1, AZ3 and AZ5 since the materials were different.

<table>
<thead>
<tr>
<th>Table 1. The proportion of different samples.</th>
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<tr>
<td>Sample</td>
</tr>
<tr>
<td>AZ1</td>
</tr>
<tr>
<td>AZ2</td>
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<tr>
<td>AZ3</td>
</tr>
<tr>
<td>AZ4</td>
</tr>
<tr>
<td>AZ5</td>
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3 Results and discussion

As it can be seen in Figures 1, 2 and 3 the endothermic peaks occur between temperatures of 300 to 600 °C with maximum loss of ignition at temperatures of 250 to 350 °C. Therefore to obtain the oxides of aluminium chloride and zinc acetate calcination on all samples were performed according to DSC results at temperature of 550 °C for 25 hrs. After calcination, XRD analysis was performed on all samples, the XRD patterns of various components are shown in Fig 4. The XRD pattern of AZ1 shows that aluminium chloride completely converted to crystal structure of gamma alumina. By incorporation zinc oxide to aluminium oxide in AZ2 the intensity of alumina peaks reduced to about half (Fig 4b). In AZ3 sample we have amorphous alumina and zinc oxide (Fig 4C) it seems addition of zinc acetate to aluminium chloride prevent formation of alumina and ZnO crystals. This behavior can be explained by further addition of ZnO to alumina in AZ4 sample as it shows in Fig 4d & e. It means participation of zinc oxide in porous alumina prevents growth of both alumina and ZnO crystals. In AZ5 with 100% ZnO amorphous structure with small peaks of ZnO crystals can be observed.
The SEM images with EDX analysis of various samples are collected in Fig 5 to 11. In Fig 5 high porous alumina with pore size of nano to micro can be observed, by adding zinc oxide to alumina in AZ2 the nano and micro porosities of alumina filled with zinc oxide particles and act like nucleated agents (Fig 6). This can be observed by EDX results. Dispersion of ZnO nano particles in high porous alumina affect to have more contact with sulphur containing gases. This behavior was evaluated by measuring surface area of different samples; the BET results are shown in Table 2. The surface area in 100% alumina (AZ1) is 199.7 g/cm², by filling the porosities of alumina with ZnO nano particles the surface area declined to 142.5 g/cm². In AZ5 with 100% ZnO surface area is 18.8 g/cm². Microstructure of AZ3 with 50% alumina and 50% ZnO is shown in Fig.3, a texture of ZnO crystals in the form of hexagonal distributed in matrix of alumina, surface area at this stage is 143.5 g/cm². Further addition of ZnO nano particles to alumina in AZ4 with 25% alumina and 75% ZnO causes to decline surface area sharply to 65.6 g/cm² and finally in pure zinc oxide the surface area is 18.8 g/cm².

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Component</th>
<th>BET (g/cm²)</th>
<th>V (cc/gr)</th>
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<tbody>
<tr>
<td>AZ1</td>
<td>Al₂O₃</td>
<td>199.7</td>
<td>46.6</td>
</tr>
<tr>
<td>AZ2</td>
<td>Al₂O₃-ZnO</td>
<td>142.5</td>
<td>33.2</td>
</tr>
<tr>
<td>AZ3</td>
<td>Al₂O₃-ZnO</td>
<td>143.5</td>
<td>33.5</td>
</tr>
<tr>
<td>AZ4</td>
<td>Al₂O₃-ZnO</td>
<td>65.6</td>
<td>15.3</td>
</tr>
<tr>
<td>AZ5</td>
<td>ZnO</td>
<td>18.8</td>
<td>4.4</td>
</tr>
<tr>
<td>HTZ-3</td>
<td>ZnO</td>
<td>15</td>
<td>2.5</td>
</tr>
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Table 2. The surface area of various samples.
The results of this study were compared with commercial zinc oxide catalyst manufactured by Topsoe (HTZ3), as it shows in Table 2 the surface area of this product is 15 g/cm² which is lowest with compare to other samples of this study [9].

The microstructures of various co-precipitated samples are shown in Figures 5 to 11. As it can be seen by introducing ZnO into the high porous alumina the hexagonal crystals of zinc oxide progressively start to grow up. In Figure 7 very sharp and flower like hexagonal crystals of zinc oxide can be observed in the matrix of alumina. Since the calcinations temperature and soaking time for all samples were same the reason for the crystal growth of ZnO by changing proportion of alumina and ZnO is not clear and it needs further investigation. In 100% ZnO in AZ5 there is no regular crystal structure for zinc oxide (Figure 11) and it seems the particle size is close to nano size. The XRD pattern of this sample in Figure 4e shows weak intensity for crystals of zinc oxide.

Figure 5. Microstructure and porous sizes of AZ1.

Figure 6. Microstructure and EDS analysis of AZ2.

Figure 7. Microstructure of AZ3.

Figure 8. Microstructure and EDS of AZ3.
Figure 9. Microstructure and EDS analysis of AZ4.

Figure 10. Microstructure of AZ4 with hexagonal crystals structure of ZnO.

In Figure 4 all the XRD graphs showing separate phases of alumina and zinc oxide, it means there is no interconnection or interface phases between these two materials. In order to understand the behaviour of alumina and zinc oxide during precipitation and calcination, FTIR examinations were performed on AZ3 sample with 75% ZnO and 25% Al₂O₃. The result of FTIR in Figures 12 is shown primary bond between ZnO-Al₂O₃. The ZnO and Al₂O₃ FTIR peaks are derived from 3 and 9 references.

Figure 11. Microstructure of AZ5 with very fine particle size.

Figure 12- FTIR spectra of ZnO-Al₂O₃.
4. Conclusions
The calcined co-precipitation of Al₂O₃-ZnO has remarkable properties from points of microstructure and activity. Zinc oxide with low surface area and porosity reacts with hydrogen sulphide and act as an absorber. By introducing ZnO to high porous alumina it was demonstrated that the surface area of ZnO indirectly can be increased. This behaviour can affect reactivity of zinc oxide with sulphur components. It means physical behaviour of alumina with chemical reactivity of ZnO can be combined to improve the catalytic properties of zinc oxide. Beside this behaviour control in growing crystals of ZnO in matrix of alumina can be obtained by different proportion of alumina and ZnO. Further investigations are needed to find out the reactivity of ZnO with H₂S in an experimental procedure.

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References