Eficient absorption of H2S by aluminum doped zinc oxide nanoparticles

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A B S T R A C T
In this study, hydrogen sulfide absorption of aluminum doped zinc oxide nanoparticles with different
aluminum concentrations (ZnxAl1−xO) has been investigated. The gas absorption rate and the samples'
structural evolutions have been also investigated by X-ray fluorescence and X-ray diffraction measure-
ments. The morphologies and particles size distribution of samples have been determined by scanning
electron microscope. The results showed that the Al doped samples have higher absorption rate in re-
spect to the pure zinc oxide. The maximum absorption rate was obtained for the sample with x = 0.01.
The average size of nanoparticles in this sample was 44 nm, which was also the lowest value among
the other samples.

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1. Introduction

Hydrogen sulfide is a toxic and highly corrosive gas [1]. The presence of
even a low amount of this gas may cause catalyst poisoning and leads to
disruption of refinery and petrochemical processes [2]. Thus, the gas
sweetening or separation of H2S from the gases is one of the important
tasks, which should be done before entering the gas to the next processes.

Nowadays, there are different methods for separating the H2S from the gas streams [3,4]. One of the most common methods of
H2S absorption is using zinc oxide as an absorber [5]. In this method, it is customary to pass the gases through a reactor which contains
zinc oxide at temperatures about 700 °C. So the H2S gas reacts with
ZnO, and produces ZnS and water [6].

In this study, it has been tried to modify the ZnO nanoparticles in
order to increase their H2S absorption ability by aluminum doping of
this compound. Thus, the absorption rates of aluminum doped zinc
oxide (AZO) nanoparticles with various aluminum concentrations
have been measured at different temperatures. The results have
been compared with H2S absorption rate of pure ZnO.

2. Materials and methods

2.1. Experimental setup

AZO nanoparticles (ZnxAl1−xO) with different aluminum concen-
trations (x = 0, 0.01, 0.03, 0.06, 0.09, 0.12) were fabricated.

The results have been published elsewhere [7]. In order to examine
the H2S absorption rate, an experimental setup was designed and
built for this purpose, which allowed the H2S gas to flow over the
samples at certain flux and temperatures. Fig. 1 shows the experimental
setup.

The setup consisted of two tube furnaces which a quartz tube
(with an approximate diameter of 2 cm) had been passed through
them. One end of the tube had been connected to a H2S generator
reservoir, and the other end had been guided to the free space.
Two furnaces had been set at the same temperatures. Because the
tube furnaces have a temperature gradient through them, in order
to make a constant temperature gas flow, the first furnace could
heat the gases to the desired temperatures. The sample had been
placed at the center of the second furnace so the H2S could pass
over it.

In order to generate H2S gas, the reaction of FeS (Alfa Aesar-
012842) with HCl based on below formula has been used.

FeS + 2HCl → FeCl2 + H2S

For establishing a proper gas flow, Ar was used as the carrier gas
with a flow rate of 5 sccm.

2.2. Experimental procedure

0.1 gr of sample was placed at the center of the second furnace. A low rate of 5 sccm Ar gas flux was established through the setup.
After 5 min (the time required to reach a steady state), 500 ml of
0.2 M of HCl was added to 3 gr of FeS in the H2S generator reservoir.
After 10 min, the quartz tube was disconnected from reservoir, and
the sample was removed from the furnace. The procedure was repeated for all samples at different temperatures of 300, 400, 500 and 600 °C.

3. Analysis

XRD measurement of samples revealed that the absorption of H2S by ZnO leads to formation of ZnS. So by measuring sulfur content of samples, or formation of ZnS compound, the H2S absorption rate can be obtained. Thus, the XRF (Bruker S4 Explorer) and XRD (Philips-PW1840) analyses were performed for samples. The shape and particle size distributions (and average particles size) of samples were also defined by SEM (Cam-Scan MV2300).

4. Results and discussions

Fig. 2 shows the XRF results of samples. As can be seen from this figure, all doped samples in all temperatures have a greater absorption rate respect to pure ZnO. The highest rate belonged to the samples with x = 0.01. This figure also shows that the absorption rate has increased in higher temperatures. An important point is that the absorption rate of the sample with x = 0.01 at 400 °C has a greater value than pure ZnO even in 600 °C.

Fig. 3(a), (b) and (c) shows the X-ray diffraction results for samples after absorption of H2S in 400, 500 and 600 °C respectively (XRD results for other temperatures are not shown here). Increasing of the (002) peak intensity which belongs to the highest intensity peak of ZnS respect to pure ZnO can be seen easily in this figure. The variation of the peak height against aluminum concentrations at different temperatures has been shown in Fig. 3(d) which are compatible with the XRF results (Fig. 2).

In fact by inserting the Al atoms in the ZnO crystal lattice can disturb the lattice order, and cause crystal defects increment. Thus, the crystal lattice strength becomes weak, and so the compound needs less energy for reacting with H2S. It should be mentioned that the Al ions have an excess electron which can help in breaking of the H2S bounds and make easier reaction between H2S and ZnO.

By aluminum doping of ZnO, the Al atoms with ionic radius of 53.5 pm are substituted in the positions of Zn atoms with the ionic radius of 74 pm. Reduction in ionic radii of atoms can reduce the lattice parameters and thus can lead to a reduction in particles size [7]. This effect was observed for our samples and the average particles size of samples against Al concentrations is illustrated in Fig. 4. As can be observed from Fig. 4, by increasing the Al concentration from 0.01, the lattice parameters and particle sizes increase. We believe there is another effect due to an excess charge of Al with respect to Zn, which competes with this factor. These excess charges may cause a repulsion force in the crystal lattice of ZnO. That is why we observe lattice parameters growth and thus particles’ size growth by increasing Al concentration in the crystal lattice (Fig. 4). It should be noted that even for the sample with x = 0.12, the average particle size was smaller than that of the pure ZnO.

Reduction in particles size means increment in surface to volume ratio (SVR). It is obvious that, the sample with higher SVR should have greater H2S absorption rate. Since the sample with x = 0.01 has the smallest average particles size (44 nm), thus this sample has highest SVR and so the highest H2S absorption rate among the others.

Another phenomenon which may have impact on the H2S absorption is the gas absorption in surface or interface of ZnO grains. Straumal et al. have shown that the solubility of an impurity in a poly crystal increases with decreasing grain size, because the impurity dissolves not only in the crystallite bulk but also on the grain boundaries [8,9]. The thickness of these boundary layers depends strongly on the concentration of dopant. It could be supposed that these surface or interface layers may be able to absorb the H2S gas. Since the sample with x = 0.01 has the smallest particle size, this phenomenon may be responsible for observing increase in gas absorption else.

5. Conclusion

Based on our results, doping of zinc oxide with aluminum can cause an increment in H2S absorption rate. It may be possible to have greater absorption rate at a lower temperature by Al doping of ZnO with respect to pure form of this compound. The best result was obtained for x = 0.01 in Zn0Al1−xO composition.
Fig. 3. X-ray diffraction of samples after passing H₂S gas over them at (a) 400 °C, (b) 500 °C and (c) 600 °C. (d) Evolution of (002) peak of ZnS in samples against Al concentrations.

Fig. 4. Left) Typical SEM image of samples (nanoparticles in all samples have a spherical shape). Right) Lattice parameters and average particles size of samples against Al concentrations.
References