A New Method for Sulfur Components Removal from Sour gas Through Application of Zinc and Iron Oxides Nanoparticles

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ABSTRACT: Use of zinc and iron oxide are common in the desulfurization process from natural gas. In this research, after determinations of the size and specifications through TEM and XRD for each of the metal oxides, two different size ratios were used, 0.66 for zinc oxide and 0.142 for iron oxide. Further, absorption of sulfur compounds in gas (hydrogen sulfide (H_2S), carbonyl sulfide (COS), methyl mercaptan (C_1SH), ethyl mercaptan (C_2SH), dimethyl sulfide (DMS), and carbon disulfide (CS_2) were evaluated at 26°C, 15 psi. The separation and identification processes of the sulfur components were measured by gas chromatography with a chemical luminescence sulfur detector. Results show that particle size variation in zinc oxide increased the sulfur removal from H_2, C_1SH and C_2SH from 9.4% to 15.8%, but in the case of COS, DMS and CS_2 no significant sulfur removal was observed. Further, with reduction of iron oxide particle size (from 0.140 μm to 20 nm), the sulfur removal rate increased from 37.9 to 63.1% in all of the natural gas components.

Keywords: Sulfur components, Nanoparticle, Natural gas, TEM, XRD

INTRODUCTION

There are substantial quantities of different sulfur compounds in natural gas (Smrtand & Meiler, 1986). They cause corrosion (Duan *et al.,* 2007; Perdomo *et al.,* 2002; Ren *et al.,* 2005) and have poisoning potential. Moreover, they can also be considered as a source of air pollution (Haimour *et al.,* 2005; Sekhavatjou *et al.,* 2011). According to international environmental law, sulfur compounds must be effectively removed before emission into the atmosphere (Sayyadnejad *et al.,* 2008; Sekhavatjou,*et al.,* 2008). However, natural gas is used as sources of hydrogen gas, which is applied in fuel cell, the presence of sulfur compounds in the natural gas cause poisoning of catalyst that are mostly copper, zinc and nickel (E G&G Services, 2000). To remove the sulfur compounds from natural gas, different beds are used (Jung *et al.,* 2006; Ros *et al.,* 2007; Crespo *et al.,* 2008). They should have special characteristics, including high capacity, low cost, lack of side effects and having a neutralization reaction to non-sulfur compounds (Israelson, 2004). Metal oxides with suitable condition can be used as an absorbent (Slimane

& Abbasian, 2001; Akyurtlu & Akyurtlu, 1995; Chung & Chung, 2005; Zeng *et al.,* 1999; Alonso *et al.,* 2000; Zhao *et al.,* 2007). Zinc oxide is a compound that can be utilized in the desulfurization process (Li & king, 2006; Wang *et al.,* 2008; Lee *et al.,* 2008). Due to the high percentage of zinc in the compound (80%), zinc oxide has the ability to absorb much of the sulfur compound (Sayyadnejad *et al.,* 2008), removing it from natural gas.Due to economical considerations and optimal dynamic properties, the use of iron oxide in desulphurisation processes is common (Akyurtlu & Akyurtlu, 1995; Ren *et al.,* 2009; Tseng *et al.,* 1981; Toma´s-Alonso & Palacios Latasa, 2004). Furthermore, the use of the metal oxides nanoparticles, due to their special chemical and physical properties, could significantly increase the absorption process that is directly dependent on the size of the particles and compression ability (Raveendran Shiju & Guliants, 2009). The absorbance was considerably increased by decreasing the size of the particles and increasing the contact area (Lee *et al.,* 2008; Al-Abadleh & Grassian, 2003).

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In this paper, the performance of zinc and iron oxide were measured in two different particle sizes for the purpose of absorption of sulfur compounds in natural gas (i.e. hydrogen sulfide, carbonyl sulfide, methyl mercaptan, ethyl mercaptan, dimethyl sulfide and carbon disulfide) by an oxidizing process. The results showed that the sulfur compounds of the natural gas were absorbed by reduction of zinc and iron oxide particle size.

MATERIALS & METHODS

In this research a chemical compound has been used to absorb sulfur container gas. Identification of the material characteristics used in the experimental method is very important. Structural analysis was carried out using X – ray diffraction (XRD) and transmission electron microscopy (TEM) . XRD and TEM were obtained for zinc oxide (analytic reagent grade), iron oxide (analytic reagent grade), as well as zinc oxide and iron oxide nanoparticles individually.
To investigate the amount of sulfur components removed by metal oxides, the following steps were performed.

-The amount of sulfur components (hydrogen sulfide (H_2S), carbonyl sulfide (COS), methyl mercaptan (C_1SH), ethyl mercaptan (C_2SH), dimethyl sulfide (DMS) and carbon disulfide (CS_2)) were analysed before passing the gas through the metal oxides. For this purpose, the chromatograph was examined after injection of a sulfur compound containing standard gas to the GC. After reaching the injection stability condition, the standard test method was continued.

Additionally, after assuring the stable condition of the chromatograms, which were related to the standard gas injection at the same pressure and temperature, the next step of the experiment was started by using the metal oxides. In addition, to assess and test accuracy, the standard gas testing method was repeated several times under the same conditions.

-One gram of each of the metal oxides was placed in a glass column filled with the used material (the zinc oxide, iron oxide, zinc oxide nanoparticles and iron oxide nanoparticles). The column was connected to the standard gas on one side and the GC system on the other side. Fig.1 shows a schematic diagram of the experimental setup (Li & king, 2006).

-After setting up the system, the gas containing sulfur compounds was injected into the system. The experimental conditions were 26°C with, 15 psi, it remained same throughout the experiment. After one minuet passed, gas samples were analysed using GC(Varian cp-3800 with detector SCD, sievers355) (Tuan *et al.,* 1994).

-Gas flow was controlled by two stage regulators fixed to the cylinder. The operation of analysis and separation of gas injection was completed by the experimental system. The required time for analysing considered 20 minutes, to ensure the removing of all sulfur compounds in gas from column of GC system.
-The experimental test variations included the sulfur components concentration in the gas, and they were measured before and after passing gas through the metal oxides.
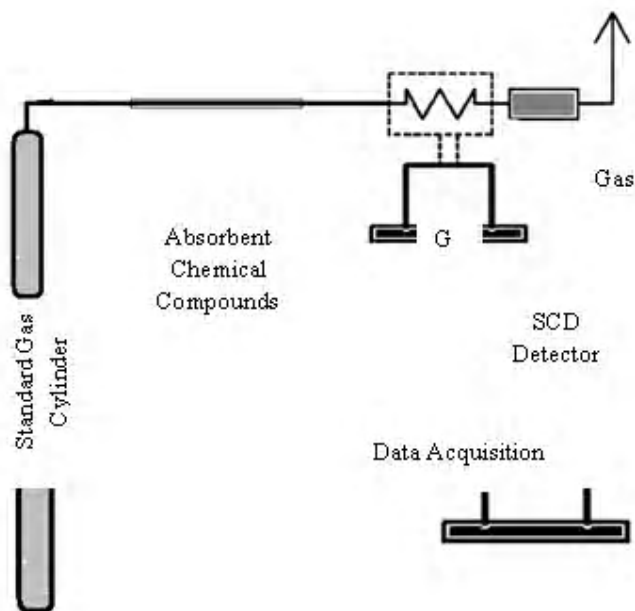

Fig. 1. schematic diagram of the experimental setup

RESULTS & DISCUSSION

XRD analysis and TEM images indicated that the sizes of the zinc oxide and iron oxide particles were 120 nm and 140 nm, respectively. Table 1. shows the characteristics of the zinc and iron nanoparticles were used for removing the sulfur components from the gas. Fig. 2 shows the X-ray diffraction pattern of the components. The TEM images of metal oxides particles are shown in Fig. 3. Table 2. shows the sulfur components concentration in the gas before and after passing through the metal oxide column. It was detected that zinc and iron oxides had high absorbance for the sulfur compound, particularly H_2S. Thus, the absorbance was considerably increased by increasing the contact area and decreasing the size of the particles.

Table 1. Characteristics of the zinc and iron nanoparticles for removing the sulfur components from the gas

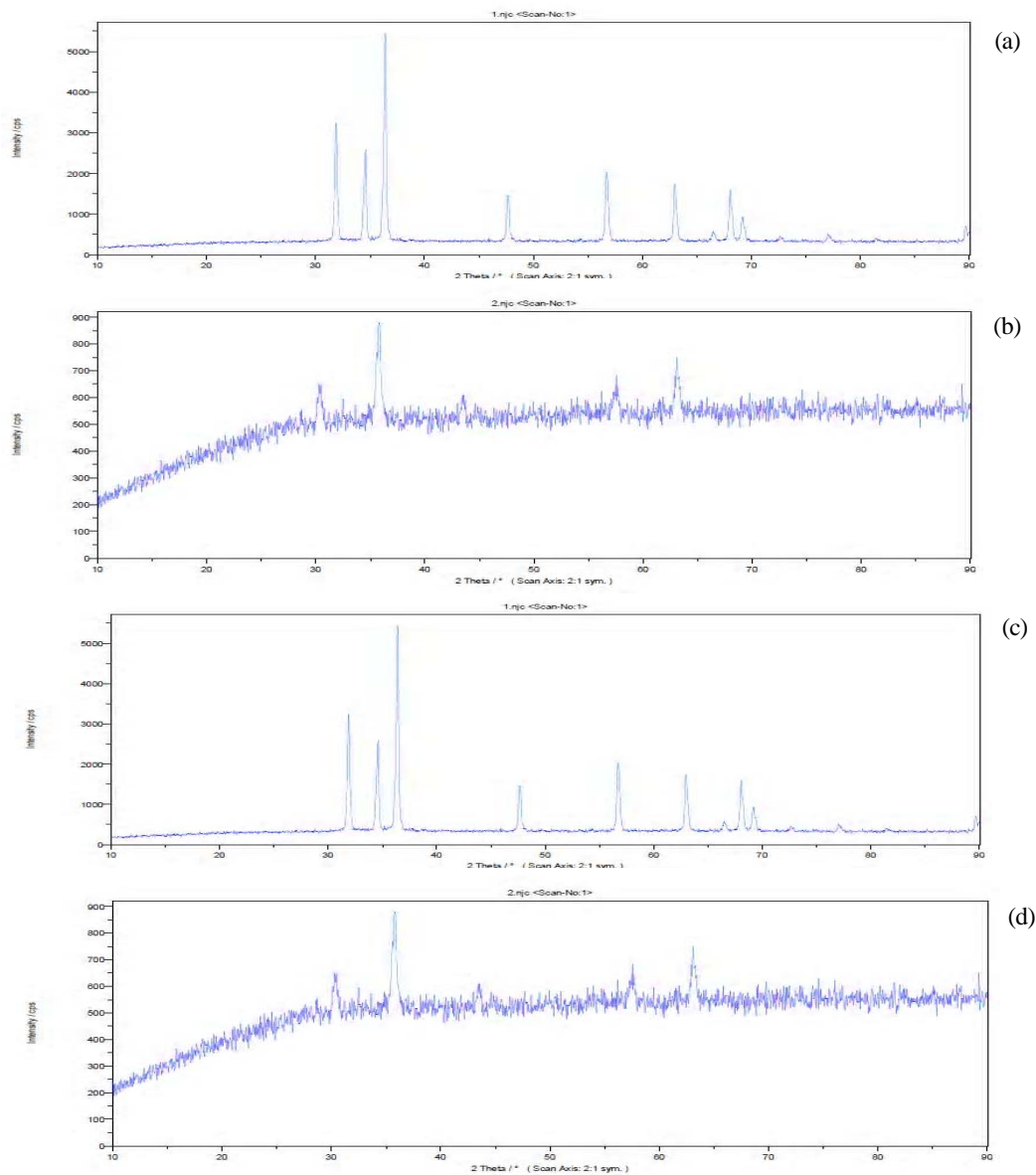| Material	Average size(nm)	morphology	Crystal structure	Surface area m^2/gr
n-ZnO	80	rod	Hexagonal Wurtzite	4.9-6.8
n-Fe$_2$O$_3$	20	spherical	rhombohedral	30

(a)

(b)

(c)

(d)

Fig. 2. X-ray diffraction patterns of the a) ZnO b) Fe$_2$O$_3$ c) n-ZnO d) n-Fe$_2$O$_3$
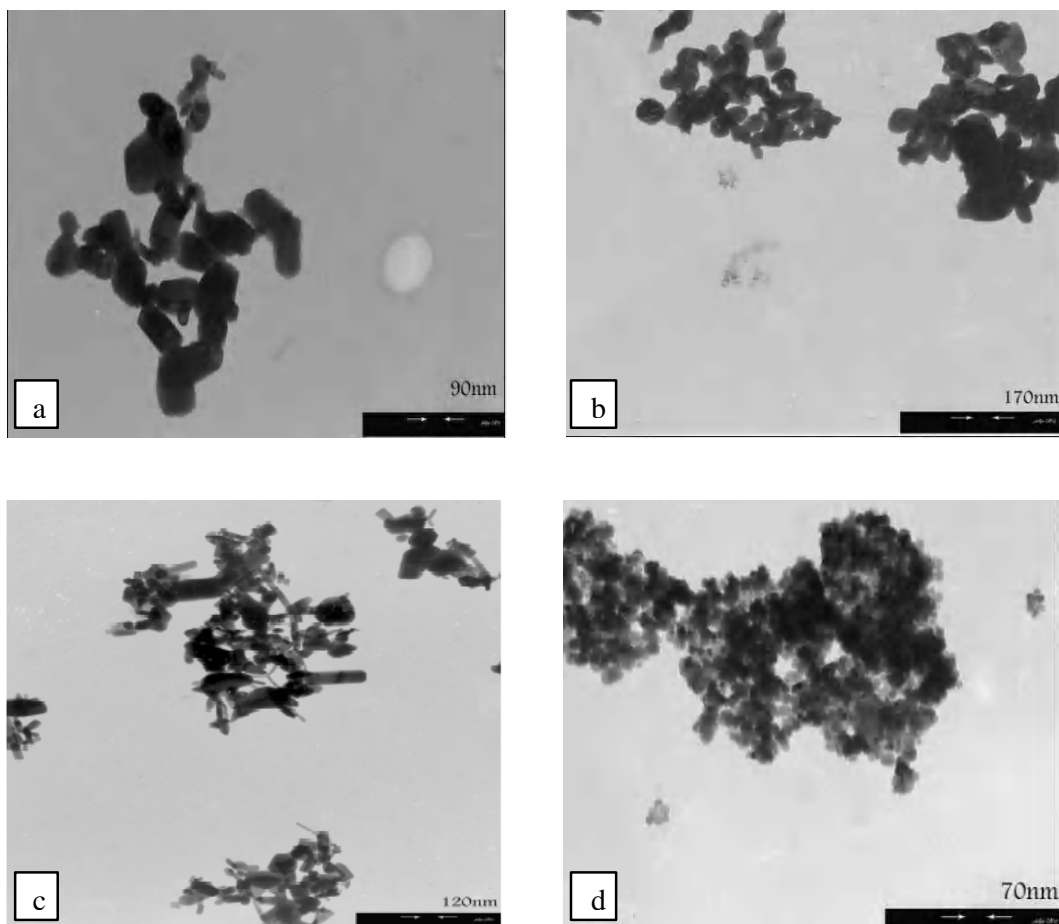
Fig . 3. TEM images of metal oxides to remove the sulfur compounds
a) zinc oxide, b) Iron oxide, c) zinc oxide nanoparticle d) Iron oxide nanoparticle

Table 2. Sulfur components concentration in the gas before and after passing through the metal oxides column

Sulfur components	The concentration before metal oxide injection into the column	The concentration after passing through the zinc oxide column	The concentration after passing through the iron oxide column	The concentration after passing through the zinc oxide nanoparticle column	The concentration after passing through the iron oxide nanoparticle column
H_2S	74	12	31	5	3
COS	65	48	60	51	28
C_1SH	19	6	13	4	2
C_2SH	19	6	13	3	1
DMS	5	3	4	3	1
CS_2	5	4	4	4	1

* values are in ppmv
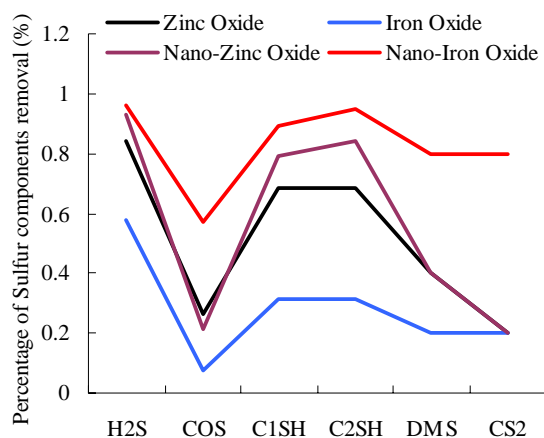
Fig. 4. Percentage of sulfur compound removal by
metal oxide particles

Table 3. Increasing removal rate with decreasing
particle size of zinc and iron oxides

Sulfur compound	percent of sulfur components removed	
	$ZnO(D_n/D_{b=0.66})$	$Fe_2O_3(D_n/D_{b=0.142})$
H_2S	9.4	37.9
COS	0	49.3
C_1SH	10.5	57.9
C_2SH	15.8	63.1
DMS	0	60
CS_2	0	60

According to the Table 2, the absorbance percentages of zinc oxide for H_2S ,COS , C_1SH, C_2SH, DMS and CS_2 were 83.8%, 26.2%, 68.4 %, 64.4%, 40% and 20% , respectively.

In the case of iron oxides, the percentages of absorbance for H_2S, COS , C_1SH, C_2SH, DMS and CS_2 were 20%, 20%, 31.6 %, 31.6%, 7.6% and 58%, respectively. As a result, the highest and lowest absorbance was related to hydrogen sulfide and carbonyl sulfide, respectively. The absorbance percentages of zinc oxide nanoparticles for H_2S, COS , C_1SH, C_2SH, DMS and CS_2 were 20%, 40%, 84.2 %, 78.9%, 21.5% and 93.2 %, respectively. In the iron oxides nanoparticles, the percentages of absorbance for H_2S,COS , C_1SH, C_2SH, DMS and CS_2 were 80%, 80 %, 94.7%, 89.5% 56.9% and 95.9 %, respectively.

As a result, the absorbance was increased in the metal oxides nanoparticle conditions, and it was mostly indicated for the compound with the least absorbance. With respect to metal oxides composition, Fig. 4. shows the percentage of sulfur compounds removal.The reduction of particle size is one of the most important parameters to investigate for the removing of sulfur compounds by metal oxides. It appears to relate to the ratio of the nanoparticles to the metal oxide particles.

In this paper, the ratio of D_n/D_b for zinc oxide and iron oxide was 0.66 and 0.142, respectively. Hence, Table 3 presents the percent of sulfur compounds removed (difference of the removal ratio of metal oxides nanoparticle to metal oxides particle) for the iron and zinc oxides.It is concluded that, with reduction of particle size, the absorption rate of sulfur compounds was increased; furthermore, the increase depended on the compound type. This process applies for compounds such as hydrogen sulfide, methyl and ethyl mercaptan. However, the reduction of particle size of carbonyl sulfide, dimethyl sulfide and carbon disulfide did not affect adsorption rate. Therefore, there is no significant difference between absorption rates by particle size for zinc oxide and zinc oxide nanoparticles. However, positive relation exists between absorption rate and reduction of particle size in iron oxide (Table 3).

CONCLUSION

Through 33% reduction of zinc oxide particle size, removal of hydrogen sulfide, methyl and ethyl mercaptan was increased by 9-16%. In the case of the other considered sulfide compounds, there was no significant relationship between reduction of particle size and removal rate. A long with much other research, this result indicates the poor performance of zinc oxide for the absorption of the carbonyl sulfide, dimethyl sulfide and carbon disulfide (Li & king, 2006). In the case of iron oxide, through 88% reduction of particle size , the removal rate of sulfur compounds was 33-37%. In contrast to zinc oxide, the reduction of particle size in iron oxide led to the elimination of the sulfur compounds in low temperatures by 49-66%. Husein M. et al. (2010), have reported similar results (Husein *et al.,* 2010).

Generally, this research reveals that zinc and iron oxide nanoparticles can be used to remove sulfide compounds in gas (concentration >100 ppm). In fact, these compounds can be used as a complement in the sour gas sweetening process, which was initially intended to reach the sulfur compounds and decrease them to less than 100ppm. This leads to a decrease in the amounts of hydrogen sulfide, which is the output of the combustion process of sulfur compounds and the main cause of acid rain (Al-Abadleh & Grassian, 2003). Further, metal oxides nanoparticles can be applied to remove the sulfur compounds from the fuel cells. Since,

a lesser amount of sulfur compounds would be present, fuel cells performance would be decrease less. Thus, it seems that using the absorbent to remove the sulfur compound is essential (E G&G Services, 2000; Li & king, 2006). With respect to the results, oxide nanoparticles could also be relevant to protective mask production.

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