

산화철을 이용한 H<sub>2</sub>S 제거

고 백균, 이 원록, 김 현정, 이 응무

아주대학교 분자과학기술학과

H<sub>2</sub>S Desulfurization Using Iron Oxide Sorbent

B. K. Kho, W. R. Lee, H. J. Kim, W. M. Lee

Department of Molecular Science and Technology, Ajou University

1. Introduction

A great deal of research has been carried out in the last twenty some years to develop high temperature desulfurization. For example, the efficiency of advanced power generation processes based on the integrated gasification combined cycle (IGCC) can be increased significantly with high temperature desulfurization. Much of the recent high temperature desulfurization research has concentrated on zinc-based sorbents such as zinc ferrite(ZnFe<sub>2</sub>O<sub>4</sub>) and zinc titanate(ZnO · xTiO<sub>2</sub>) due to its thermodynamic advantage in capturing H<sub>2</sub>S molecules.

Although iron oxide is also capable of reacting with H<sub>2</sub>S at high temperatures, the thermodynamics are less favorable than that for the ZnO-H<sub>2</sub>S reaction. At high temperature above 500°C the oxide undergoes phase transition to a much inefficient form like FeO.

In spite of less efficient desulfurization performance, iron-based sorbents can be superior in the regeneration portion of the cycle. Direct formation of significant amounts of elemental sulfur has been reported when FeS was regenerated in an H<sub>2</sub>O-O<sub>2</sub> atmosphere[1]. And it is also reported that zinc-based sorbents mixed with iron oxide show better resistance to reduction and vaporization than pure zinc oxide[2].

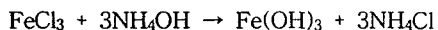
In this presentation, we report some preliminary data about the desulfurization using iron oxide sorbent. We used both commercially available iron oxide and home-made nano-structured iron oxide. We also compared the desulfurization efficiency of the sorbent when a thermal method was employed to that by a plasma-enhanced process. Plasma method is particularly attractive in accelerating chemical reactions that should be carried out at low temperature.

2. Experimental

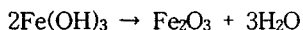
2.1 The preparation of fine iron oxide powder

The Fe<sub>2</sub>O<sub>3</sub> powder was prepared by a plasma treatment of iron hydroxide fine powders. Iron(III) chloride(FeCl<sub>3</sub> · 6H<sub>2</sub>O) was dissolved in distilled water to give a desired concentration(0.1 M). Then ammonia solution(25%) was added slowly into the FeCl<sub>3</sub> · 6H<sub>2</sub>O solution. In this process, the ammonia solution(25%) was employed primarily for adjusting the pH so that a controlled precipitation can occur. The NH<sub>3</sub>

solution(25%) was added to the solution to make its pH higher than 9. Following the adjustment of pH, brown powders( Fe(OH)<sub>3</sub>) precipitated in a clear NH<sub>4</sub>Cl solution.



The powders were separated from the NH<sub>4</sub>Cl solution by decantation or a filter paper. The powder was washed ten times in distilled water. The fine powders were obtained by drying the hydroxide precipitants at 60~70°C and grinding them. The Fe<sub>2</sub>O<sub>3</sub> powders were then obtained under plasma environment to facilitate the reaction.



## 2.2. The high temperature desulfurization and regeneration process

The high temperature reaction system is shown in Fig.1. This process was carried out in a reactor made of quartz. A quartz wool was used as a sample support. First, the fine iron oxide powder was placed in the reactor. The reactor was then filled with nitrogen gas after evacuating it first. The reactor gas, a gas mixture of hydrogen sulfide and nitrogen, was then fed into the reactor using mass flow controller. The concentration of H<sub>2</sub>S in the mixture was adjusted to be 100ppm, 1,000ppm or 10,000ppm. The mixture was allowed to flow for 2hrs with the temperature of the system maintained at 200°C. The exhaust gas from the reactor was collected and analyzed with GC(HP6890/FPD) and FTIR(Nicolet Magna-IR). The treated solid sample was characterized by X-ray diffraction(XRD) and scanning electron microscopy(SEM). The sulfurized iron sample was treated with oxygen gas to regenerate iron oxide with the temperature maintained at 600°C. The treated sample was again characterized by XRD and SEM.

## 2.3. The RF Plasma Process

The RF plasma reaction system is shown in Fig. 2. The plasma was generated by a capacitive discharge through two copper electrodes placed around the external surface of the reactor. As the power source, 13.56MHz RF generator was used with a proper matching network. The sulfurized iron sample was treated at room temperature with oxygen plasma to regenerate iron oxide. First, the reactor was pumped down to ~10<sup>-3</sup>torr. The oxygen gas was introduced into the reactor at 10sccm flow rate with the help of a mass flow controller. The reaction pressure was maintained at 10torr.

# 3. Results and Discussion

## 3.1. Thermodynamic analysis

Iron oxide reacts with H<sub>2</sub>S through many different chemical paths. Three possible paths and the change of thermodynamic values along these paths are summarized in Table 1.

Table.1

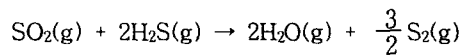
Path	$\Delta H^\circ$ (kJ)	$\Delta S^\circ$ (kJ · K <sup>-1</sup> )	Temperature for negative $\Delta G$ (K)
( I ) Fe <sub>2</sub> O <sub>3</sub> (s) + 2H <sub>2</sub> S(g) → 2FeS(s) + 2H <sub>2</sub> O(g) + 1/2O <sub>2</sub> (g)	190	79.1 × 10 <sup>-3</sup>	2400
( II ) 2Fe <sub>2</sub> O <sub>3</sub> (s) + 7H <sub>2</sub> S(g) → 6FeS(s) + SO <sub>2</sub> (g) + 7H <sub>2</sub> O(g)	44.4	112 × 10 <sup>-3</sup>	397
( III ) 9Fe <sub>2</sub> O <sub>3</sub> (s) + H <sub>2</sub> S(g) → 6Fe <sub>3</sub> O <sub>4</sub> (s) + SO <sub>2</sub> (g) + H <sub>2</sub> O(g)	178	251 × 10 <sup>-3</sup>	709

It is seen from Table 1 that path II is a favorable path to form FeS even at low temperature around 400K. As temperature rises above 700K, Fe<sub>2</sub>O<sub>3</sub> undergoes phase transition to Fe<sub>3</sub>O<sub>4</sub>. At even higher temperature there is a possibility that Fe<sub>3</sub>O<sub>4</sub> transforms to FeO. The thermodynamic values for the reactions of FeS with O<sub>2</sub> or H<sub>2</sub>O are summarized in Table 2.

Table 2.

Reaction	$\Delta H^\circ$ (kJ)	$\Delta S^\circ$ (kJ · K <sup>-1</sup> )
2FeS(s) + $\frac{7}{2}$ O <sub>2</sub> (g) → Fe <sub>2</sub> O <sub>3</sub> (s) + 2SO <sub>2</sub> (g)	-1230	-330 × 10 <sup>-3</sup>
3FeS(s) + 4H <sub>2</sub> O(g) → Fe <sub>3</sub> O <sub>4</sub> (s) + 3H <sub>2</sub> S(g) + H <sub>2</sub> (g)	74.9	9.87 × 10 <sup>-3</sup>
2Fe <sub>3</sub> O <sub>4</sub> (s) + $\frac{1}{2}$ O <sub>2</sub> (g) → 3Fe <sub>2</sub> O <sub>3</sub> (s)	-232	-126 × 10 <sup>-3</sup>

Besides the reactions shown in Table 2, an additional reaction can take place if the ratio of SO<sub>2</sub> to H<sub>2</sub>S is proper,



From the above reaction, the desulfurization of FeS in the presence of H<sub>2</sub>O and O<sub>2</sub> can yield elemental sulfur rather than SO<sub>2</sub>.

### 3.2. Sulfurization of Fe<sub>2</sub>O<sub>3</sub>

When Fe<sub>2</sub>O<sub>3</sub> particle (from aldrich, <5μm, +99%) reacted with H<sub>2</sub>S (100ppm) for 2hrs at 600°C, the XRD analysis of the particle(Fig. 3) showed that it underwent phase transition to Fe<sub>3</sub>O<sub>4</sub>, rather than to FeS, as predicted by the thermodynamic values shown in Table 1.

But when the concentration of H<sub>2</sub>S was raised to near 10,000ppm, the sample

was transformed into FeS while other experimental conditions were kept the same as in the previous experiment. Thus, it is seen that the sulfurization process is sensitive to H<sub>2</sub>S concentration. A very fine Fe<sub>2</sub>O<sub>3</sub> particles prepared by a combined process of sol-gel and the plasma method was transformed to FeS when temperature was maintained at around 200°C.

### 3.3. Desulfurization of FeS

A large particle size FeS (from aldrich, <150 μ, 99.9%) powder was not desulfurized when the oxygen plasma method was employed as the oxidant. It is believed that the desulfurization only occurred at the very surface of the powder. But the same FeS powder (from aldrich, <150 μ, 99.9%) was desulfurized using a thermal method when temperature was maintained at 600°C. This may be due to the fact that the oxide diffusion into the inside of the particle was facilitated at elevated temperature. Thus the plasma method is not a suitable method for treating particles of large size.

When the fine home-made FeS particle was treated in O<sub>2</sub> plasma at room temperature, the gas analysis of the output gas and XRD analysis of the solid sample showed that a substantial portion of the FeS powder was desulfurized.

## 4. Conclusions

Iron oxide powder reacts with H<sub>2</sub>S more efficiently to form FeS when the reaction temperature is kept below 500°C. Very fine iron oxide powder can be prepared by a combined process of sol-gel and a plasma excitation method, probably due to excitation of the solid sample by excited gaseous molecules. Such prepared powder showed excellent performance in both sulfurization and desulfurization.

## 5. Reference

1. J. D. White, F. R. Groves, D. P. Harrison, *Catalysis Today*, **40**, pp 47-57 (1998).
2. L. D. Gasper-Galvin, A. T. Atimtay, R. P. Gupta, *Ind. Eng. Chem. Res.*, **37**, pp 4157-4166 (1998).

## Acknowledgements

This work was supported by "Coal Gasification" program managed by the Korea Energy Management Corporation and sponsored by the Ministry of Commerce, Industry and Energy of the Republic of Korea.

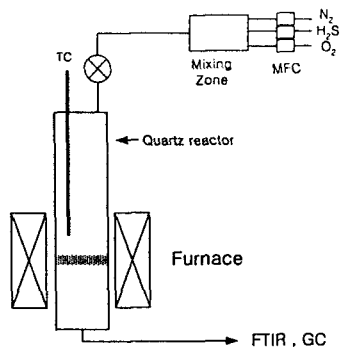


Fig.1. The experimental set-up for high temperature desulfurization process

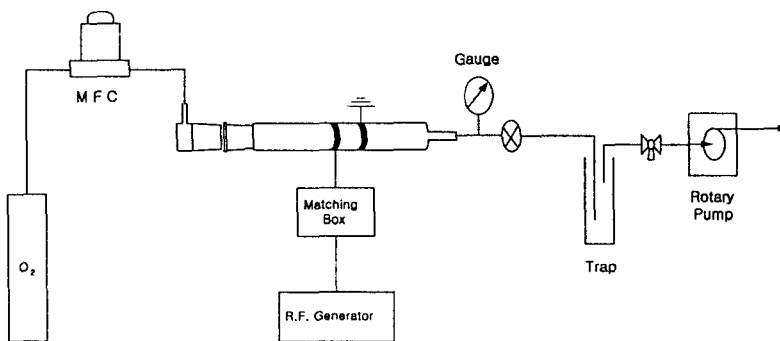
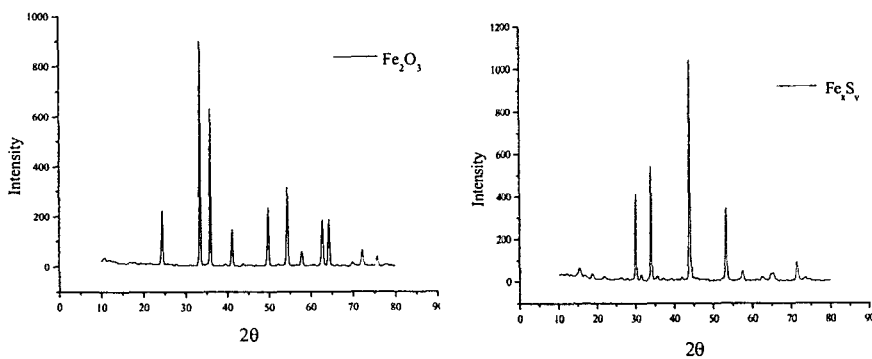


Fig.2. The experimental set-up for RF plasma process



(a) ( $\text{Fe}_2\text{O}_3$ , <5micron, +99%)

(b) Sulfurized iron oxide ( $\text{Fe}_x\text{S}_y$ )

Fig.3. XRD analysis of the sulfurized  $\text{Fe}_2\text{O}_3$  sample