Development of Porous Sorbents for Removal of Hydrogen Sulfide from Hot Coal Gas

—I. Additive Effect of Sorbents for the Removal of Hydrogen Sulfide—

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고온석탄 가스에서 황화물을 제거하기 위한 다공성 흡착제의 개발

— I. 황화수소가스 흡착제의 첨가물 효과 —

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요   약

석탄유도가스에 포함된 황화수소를 제거시킬 흡착제를 개발하기 위하여 알칼리 토금속, 천이원소 및 아연(Zn^{2+})의 이온반경보다 이온반경이 작은 금속산화물을 산화아연에 첨가시켜 다공성 흡착제를 제조하였다. 600℃에서 이들 첨가시료를 2.09 vol.% 황화수소와 질소가스 혼합기체로 반응시켜 초기속도를 측정하고, 같은 온도에서 사용된 흡착제를 공기로 재생시켰다. 사용된 금속산화물 첨가 흡착제중에서 CaO, TiO_2, Fe_2O_3, CuO, Ga_2O_3 및 Li_2O가 ZnO 흡착제의 초기속도를 증가시켜 첨가제로 사용할 수 있음을 보였다.

I. INTRODUCTION

A number of studies on the removal of hydrogen sulfide in coal gasification process or combined cycle power generation using the coal gas have been reported over the last decade. Most of these researches were concerned with the methods of reducing the sulfur content from several thousand parts per million (ppm)

to a few hundred parts per million. Particularly the sulfur content must be reduced to only 1 ppm for molten carbonate fuel cell power generation.

Primarily, various metal oxides and their mixtures have been studied as sorbents for removal of H_2S. Deo and Dalla Lana[1] have studied on the adsorption of H_2S and SO_2 on the alumina and zeolite, and Liu et al.[2] have studied the adsorption of H_2S and SO_2 on y-alumina and IR studies of the surface reaction. Tamhankar et al.[3,4] investigated the reactions of 45 wt.% Fe_2O_3 with a hot gas containing H_2, CO and H_2S and repoted that initial fest reduction of Fe_2O_3 to spongy iron, which reacted slowly with the H_2S to form iron sulfide. Also they reported that in the regeneration experiment[4,5] of the used Fe_2O_3, FeS reacted with air to form Fe_2O_3 and SO_2 and this sorbent can be used continuously. Schrodt and Mohan have studied fuel gas desulfurization in fluidized beds of gasifier waste ashes containing iron oxides and developed the reaction model with diffusion of H_2S through unreacted layer. Grindley and Seinfield[7] reported that zinc ferrite has good results as sorbent for removal of H_2S and has good regenerability in a series of studies at Morgantown Energy Technology Center. In 1985 Yumura and Furimisky[8] compared H_2S adsorption capacity of CaO, ZnO and Fe_2O_3, and suggested that Fe_2O_3 has the best capacity. Kocafee et al.[9] compared the sulfidation rate of CaO, MgO and ZnO with SO_2 and SO_3. Bogarello et al.[10] represented the photocomposition of H_2S in aqueous alkaline media catalyzed by RuO_2-loaded alumina in the presence of cadmium sulfide by application of the inter-particle electron transfer mechanism. Anderson et al.[11] reported that zinc aluminate and zinc chrominate sorbents have resonable sulfur removal capacities and good regeneration characteristics and give good sulfer yields, and also cobalt titante, zinc oxide, cobalt oxide/silicate sorbents among the used sorbents such as cobalt aluminate, manageous oxide, iron chromate, iron orthosilicate, cobalt titanate and zinc oxide, can be used as sorbents which increase the amount of elemental sulfur while minimize that of SO_2 in the sulfur recovery process. Larishnan et al.[12] evaluated the thermodynamic equilibrium and explained the formation of sulfate when the used sorbents such as ZnO, Fe_2O_3, $CuO-Al_2O_3$, $CuO-Al_2O_3$, and $CuO-Al_2O_3-Fe_2O_3$ as regenerable sorbents. The results indicated that $CuO-Fe_2O_3$ $CuO-Al_2O_3$ and $Al_2O_3-CuO-Fe_2O_3$ were good sulfur capture capacity and regenerability. In addition, numerous studies for sulfur removal from coal gas have been reported.[14-17]

When the above researches were reviewed all the sorbents have problems in terms of economy. Namely, as result of comparison ZnO to Fe_2O_3 which are recognized as probable sorbents, Fe_2O_3 has faster reaction rate then ZnO but equilibrium composition of H_2S is higher than ZnO, in the other hand ZnO is restricted by loss of surface area and the adsorption capacity and regenerability of ZnO is not good. It has been revealed that the characteristic of sorbents such as mechanical strength, as well as the physicochemical properties, changes.

Therefore, the objective of the present work is to develop the new sorbents and additives for ZnO which improve the chemical

property such as reaction rate and adsorption capacity, mechanical strength and regenerability.

II. Materials and Methods

1. Sorbent selection

Recent research has shifted from pure oxides to mixed oxides with the goal improving sorbent performance. The sorbent and additives used in this work were selected as follows:

1) They must be nontoxic and aqueous salts and should meet one of the two following conditions.
2) Ionic radius of additives must be equal to or smaller than that of basic sorbent.
3) The materials must be one of transition elements or alkaline earth metals with outermost electron of s-orbit.

The first condition is to protect the pollution and to be complete mixing during the preparation of sorbents and the second condition is based on the general theory of solid chemistry which claim that ionic radius of depant is smaller than that of basic material. The third condition is proposed on the basis chemical and physical characteristic of transition elements and alkaline earth metal differed from those of others. Materials which satisfy the above mentioned 3 conditions, are listed in Table 1.

Table 1. Physical and Chemical Properties of Sorbent(ZnO) and Additives

	sorbent & additives	ionic radius	electronic configuration	crystalline form	original formulas	formular weight
Alkaline earth metal	MgO	0.65	········$3s^2$	rhombic	$Al(NO_3)_3 \cdot 9H_2O$	375.13
	CaO	0.99	········$4s^2$	monoclinic	$Ca(NO_3)_2 \cdot 4H_2O$	236.15
	SrO	1.13	········$5s^2$	monoclinic	$Sr(NO_3)_2 \cdot 4H_2O$	283.69
	BaO	1.35	········$6s^2$	hexagonal	$Ba(NO_3)_2 \cdot H_2O$	247.37
Transition metal	TiO$_2$	0.68	········$3d^2s^2$	rhombic	$Ti[OCH(CH_3)_2]_4$	284.26
	Cr$_2$O$_3$	0.65	········$3d^54s^1$	monoclinic	$Cr(NO_3)_2 \cdot 7\frac{1}{2}H_2O$	373.13
	MnO	0.80	········$3d^54s^2$	monoclinic	$Mn(NO_3)_2 \cdot 6H_2O$	287.04
	Fe$_2$O$_3$	0.67	········$3d^64s^2$	rhombohedral	$Fe(NO_3)_3 \cdot 6H_2O$	349.97
	CoO	0.82	········$3a^74s^2$	monoclinic	$Co(C_2H_3O)_2 \cdot 4H_2O$	249.08
	NiO	0.78	········$3d^84s^2$	monoclinic	$Ni(NO_3)_2 \cdot 6H_2O$	290.81
	CuO	0.96	········$3d^{10}4s^1$	rhombic	$Cu(NO_3)_2 \cdot 6H_2O$	295.64
	ZnO	0.74	········$3d^{10}4s^2$	tetragonal	$Zn(NO_3)_2 \cdot 6H_2O$	sorbent 297.47
Others ($< \gamma_{Zn}^{2+}$)	Al$_2$O$_3$	0.50	········$3s^24p^1$	rhombic	$Al(NO_3)_3 \cdot 9H_2O$	375.13
	Ga$_2$O$_3$	0.62	········$4s^24p^1$	rhombohedral	$Ga(NO_3)$	255.73
	Li$_2$O	0.60	$2s^1$	cubic	$LiNO_3 \cdot 3H_2O$	122.99

2. Sorbent preparation

Sorbent preparation was carried out by a special method for synthesizing highly porous mixed oxides, and the procedure is as follows:

1) Mixing two compounds in defined amount
2) Add some moles of organic polyfunctional acid as blowing agent
3) Completely dissolve every compound in minimum distilled water using magnetic stirrer for 40 min.
4) After every compound has dissolved fully, keep the solution in air oven at 65-70°C for 4-8hr.
5) When the mixture begins to get viscous, transfer it to vacuum oven and to be rapidly dehydrated in there at 70°C for 24hr
6) Put the mixture in high temperature furnace and calcine at 550°C under O_2 flow for 3-6hr.

3. Experimental apparatus and procedure

APPARATUS: The experimental apparatus as shown in Fig. 1 consisted of a quartz tube, 2.54cm e.d. x 40cm length. The platinum sample basket containing 5.0mg of 20-35 mesh size sorbent is suspended by a fine platinum wire attached to the top of the microbalance beam and temperature is automatically controlled by a CA-thermocouple located just upper the sample basket. As shown Fig. 1, the gases are seperately introduced to the reactor through two side tubes. The reactive gases mixed with the nitrogen enter through a side tube located just upper the furnace, and the nitrogen enters through the balance mecha-

1. Hydrogen deoxo purifier
2,4,6,7. Zeolite trap
3. Connect to the other System
5,8. Deoxygen trap
9. Thermocouple
10. G. C.
11. H_2SO_4 bottle
12,18. Soap film flow meter
13. Furnace
14. Sample
15. Preheater
16. Preheater
16. Three – way valve
17. Microbalance

∅ : Regulator
⊗ : On -off valve
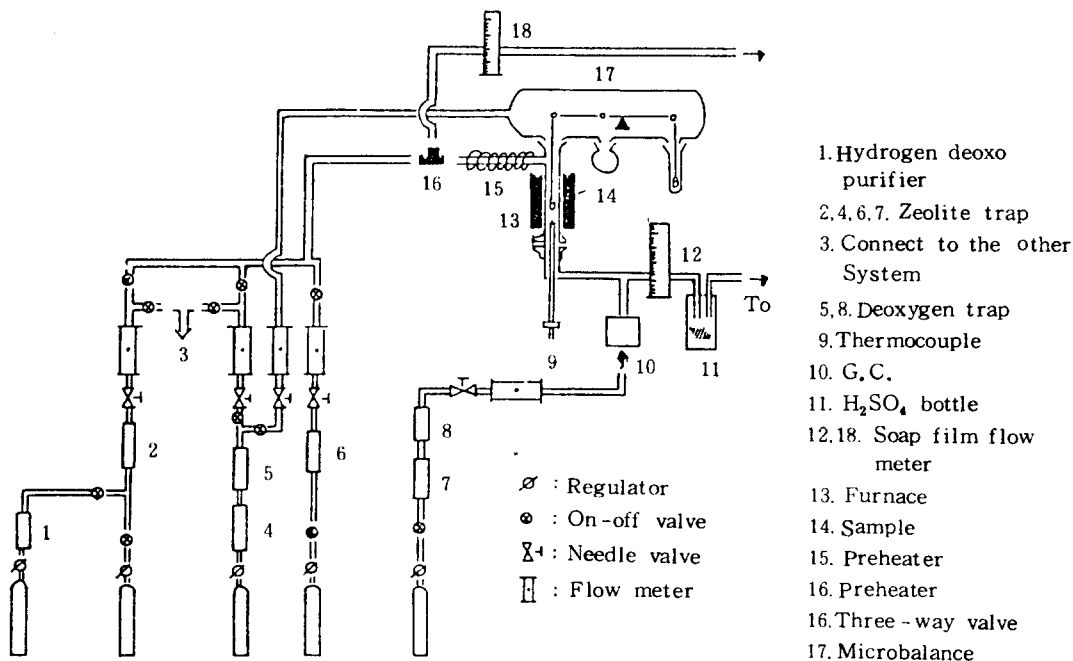⋈ : Needle valve
Ⅱ : Flow meter

Fig. 1. Schematic Diagram of Experimental Apparatus

nism housing from before the run to an hour after the end of the run in order to prevent back flow of the reactant gases which are extremely corrosive, to the TGA balance section. The outlet gases are vented from the bottom of reactor and a part of those are introduced to gas chromatography to analyze the composition of the product gases. The O_2 cylinder is attached to regenerate the used sorbents and the flow rate of introducing gases are measured with a calibrated rotameter. **PROCEDURE:** The balance is zeroed and the sorbent of 5.0mg is placed on the platinum pan, and then, the balance section of the assembly is constantly purged with netrogen flowing at a known flow rate and the reaction tube is heated to the desired temperature. When steady stage is maintained at desired temperature (300-700°C) adjust zero point of balance then desired composition of the gas mixture of hydrogen sulfide (0.5-2.5 vol.%) and nitrogen is introduced to the reaction tube simaltaneously start TGA-recorder and record the amount of adsorption of hydrogen sulfide. The introducing gas is switched from the reactant gas mixture to nitrogen as soon as the reaction is completed, and then the reaction system is purged by nitrogen above an hour.

The outlet gas line is connected to gas chromatography (Shimadzu, GC-4C, PT) to analyze the composition of the vent gas. The used gas chromatography is equipped with a 3m x 0.5mm o column packed with chromosil 310 and flame photometric detector is attached.

Table 2. Experimental Results of the Additive Sorbents

Sorbent designation	Sorbent*	Suface area (m^2/g)	Solid solution (S. S.)	Intial rate of sulfidation (mg/min)	Normalized regeneration time ($t_R/t_R{}^*$)
A	MgO–ZnO	8	None	0.074	
B	CaO–ZnO*	8	None	0.115	0.9
C	BaC–ZnO	6	None	0.063	
D	TiO_2–ZnO	29	Zn_2TiO_4	0.204	0.8
E	Cr_2O_3–ZnO	7	None	0.064	
F	MnO–ZnO	7	?	0.070	
G	Fe_2O_3–ZnO	14	$ZnFe_2O_4$	0.990	0.90
H	CoO–ZnO	9		0.061	
I	NiO–ZnO	6	None	0.072	
J	CuO–ZnO	11	None	0.157	0.95
K	Al_2O_3–ZnO	19	None	0.075	
L	Ga_2O_3–ZnO	18	?	0.106	0.9
M	Li_2O–ZnO	23	?	0.287	0.7
N	Pure ZnO	8		0.077	1

* All additive's content are same in 0.5 atomic % (2.0 atomic % for CaO)

III. Results and Discussion

The basic sorbent being used in this experiment was ZnO and additives were Li_2O and other 14 metal oxides. These metal oxides are listed in Table 2.

Generally the range of temperature during the experiment of adsorption of hydrogen sulfide is mostly 400-750°C but in this study by utilizing the fact that reaction rate is accelerated when small amount of other materials are added to the additives initial reaction rate only is compared at 600°C since the purpose of this study is to develop sorbert which can improve the reaction rate of basic sorbents such as ZnO or Fe_2O_3.

In Fig. 2 initial reaction rate of pure ZnO according to the flow rate of mixed gas at 600°C is indicated. As shown in the figure at the point where flow rate of mixed gas exceeds 140 cc/min the change of initial reaction rate can not be seen much therefore in this experiment flow rate of mixed gas with 2.09 vol% of content of hydrogen sulfide was fixed to 140cc/min and experiment is undertaken at 600°C.

In Table 2 14 kinds of mixed sorbents being prepared by adding 0.5 atomic% of additive respectively to basic sorbent, ZnO, surface area of basic sorbent, ZnO, formation of solid solution and value of initial reaction rate of hydrogen sulfide are recorded.

MgO-ZnO with addition of 0.5 atomic% of MgO to the Crystal structure and 7 other mixtures were found as existing in their original state in respect of metal oxides when analysed by X-ray diffractor. But with MnO-ZnO, CaO-
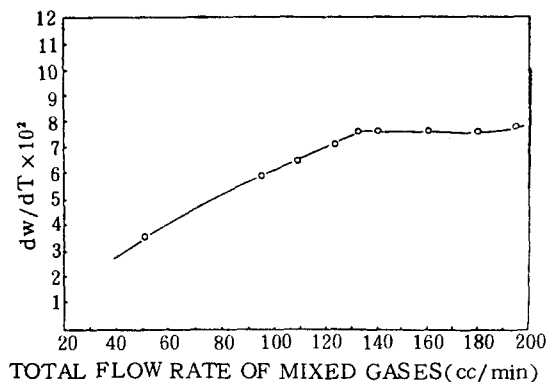

Fig. 2. Influence of Total Gas Flow Rate of the Mixed Gases on the Initial Sulfidation Rate of Pure Zine Oxide at 600°C
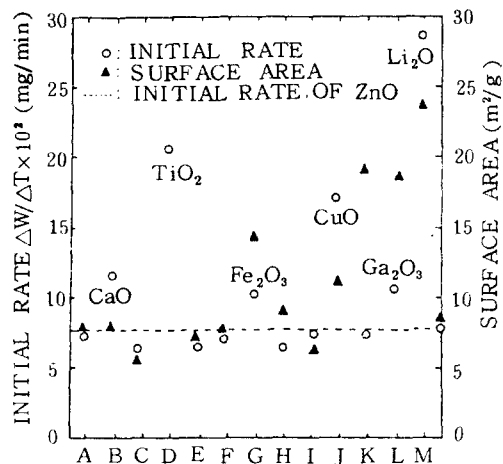

Fig. 3. Initial Sulfidation Rate and Surface Area of the Additive Sorbents

ZnO, $Ga_2^2O_3$-ZnO and Li_2O-ZnO property of metal oxides were vague and there was no evidence for the formation of solid solution. On the other hand, with TiO_2-ZnO $ZnTiO_4$ appeared and with Fe_2O_3-ZnO solid solution of $ZnFe_2O_4$ appeared.

In Fig. 3 surface area indecated in Table 2 and initial sulfidation reaction rate have

been described.

Initial sulfidation reaction rate indicated here is the result of experiment undertaken with flow rate of mixed gas being fixed at 140cc/min (2.09 vol%)

For convenience in finding out extent of increase and decrease of initial reaction rate in comparison with that of ZnO, the pure basic sorbent reaction rate of pure ZnO is shown by dotted line.

As shown in the figure, the sorbent with adsorption of MgO, BaO, Cr_2O_3, MnO, CoO, NiO and Al_2O_3 at 0.5 atomic % the sorbent either has similar value with that of initial rate of pure ZnO or lesser value thus indicating no effect of additive being felt. However in case of 2.0 atomic % CaO, 0.5 atomic % of TiO_2, Fe_2O_3, CuO, Ga_3O_3 and Li_2O compared to that of pure ZnO sorbent it functioned better in improving reaction rate. Particularly, Li_2O-ZnO sorbents has 3 times of higher rate than that of pure ZnO sorbent and with Ti_2O-ZnO. It has 2.5% of initial rate. While induction time of pure ZnO sorbent is 54 sec. induction time of Li_2O-ZnO and TiO_2-ZnO is close to zero. In comparison with initial rate of ZnO those of CaO-ZnO, Fe_2O_3-ZnO, CuO-ZnO and Ga_2O_3-ZnO are about 1.5-2 times and induction time was slightly shorter.

Induction time of sorbents with slower initial reaction time than that of pure ZnO sorbent has an approximate value of 54 sec. almost identical with that of pure ZnO. The ground of choosing amount of additive with CaO as 2.0 atomic % is based on the fact that in the sutdy by this writer on reduction of ferric oxide[17] it has been revealed that while other materials have decrease in reaction rate

with increase of amount of additive, but with CaO the effect of increase has been pronounced under 2.0 atomic % than that of 0.5 atomic %.

Also research on the existence of correlationship between reaction time and surface area however no particular point has been found. In short surface areas of sorbents such as TiO_2-ZnO, Fe_2O_3-ZnO, CuO-ZnO, Ga_2O_3-ZnO and Li_2O-ZnO are large(8.2m^2/ g) and concurrently they have higher reaction rate, but CaO−ZnO is higher than pure sorbent and surface area is same; in case of Al_2O_3-ZnO surface area is larger than that of pure sorbent by 2.4 times but initial reaction time is rather than pure sorbent.

As shown in the above, let's compare the available research result on the various effects for sulfidation reaction of pure ZnO with the results being described so far.

Under H_2S environment ZnO turns into

$$ZnO + H_2S = ZnS + H_2O$$ and absorbs H_2O. Fig. 4 shows the results of experiments on the
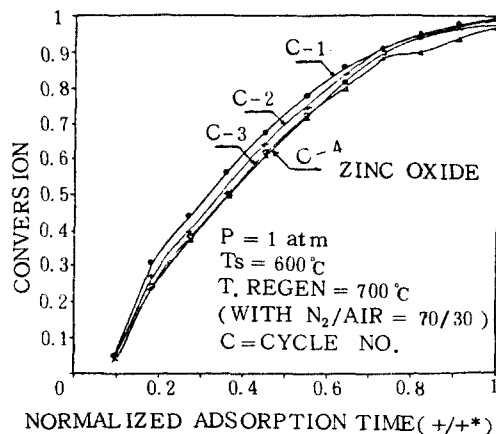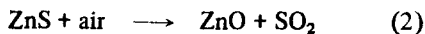

Fig. 4. Breakthrough Curve in Successive Sulfidation Cycles of Zinc Oxide [P. K. Sharma, Ind. Eng. Chem. Process Des. Dev. 25(2) 429 (1986)]

continuous cycles removing H_2S through the regenerating the sulfide reaction of ZnO and ZnS by the above-stated reaction. In the figure, t means reaction time and t* is the time upto the emission of reaction gas grom the point upon completion of reaction of ZnO with H_2S where no gas had been emitted by the reaction of H_2S initially and Gavalas called it a break-through time. And, C-1 indicates fresh ZnO, C-2 for ZnO regenerated once, and C-3 for ZnO regenerated twice in terms of the results of experiments, and in case of C-2, C-3 and C-4, it can be noted that the efficiency of sorbents is getting lower through the repetition of regenerating frequency. Observance was given to the affect of addition on the removal efficiency and regenerating effect of H_2S when CaO 2.0 at % had been added to pure ZnO. (See Fig. 5) The added CaO generally increased the removal efficiency of H_2S and also en-hanced the effect of regeneration. This type of similar tendency is taking place at all other additive samples. Table 2 shows the results on H_2S removal efficiency and regenerating effect of each additive sample acquired through such experiment. The index of H_2S removal efficiency and regenerating effect is indicated by the initial rate and normalized regeneration time as to the sulfidation of each additive sample. According to reaction (1) by means of the reaction of

$$ZnS + air \longrightarrow ZnO + SO_2 \qquad (2)$$

react pure sorbent being composed of ZnS and the time required for 90% regenerating, tr* = 30 sec. was used as standard and the proportion with the time required for 90% of regeneration after sulfidation reaction
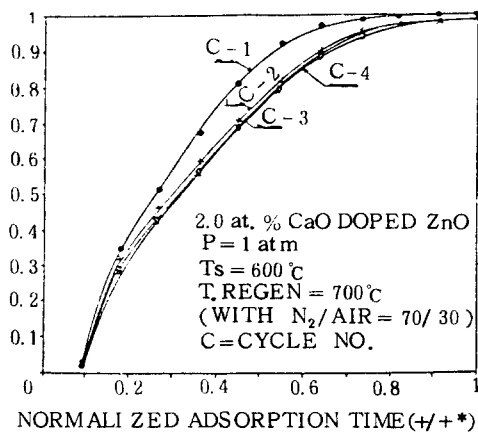

Fig. 5. Breakthrought Curve in Successive Sulfidation Cycles of Zinc Oxide

by various additive samples, i.e. tr/tr* is compared. As mentioned earlier, it can be noted that initial reacting rate rather increases and regenerating time decreases than pure ZnO at all additive samples inclusive of additions.

On the other hand, when looking at each additive sample, as the initial reacting rate is getting increased, regenerating time is getting shorter in general.

In view of these results, it is expected that the computation of the enhance of removal efficiency and regenerating time through the addition of proper dopant might help to reduce the energy required for it.

IV. Summary

Through comparison of initial sulfidation rate with addition of 14 kinds of metal oxides such as magnesium oxide to ZnO known as excellent sorbent through this study it is reveal-ed that sorbents such as CaO, TiO_2, Fe_2O_3', CuO, Ga_2O_3, Li_2O functioned as increasing initial rate of ZnO sorbent. Furthermore re-

generation time of sorbents being added to such metal oxides has been reduced than that of pure ZnO. Through the result as indicated above, it is considered that the metal oxides of the above mentioned can be used as additives.

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