

## REMOVAL OF SO<sub>x</sub> AND NO<sub>x</sub> FROM FLUE GAS WITH CERIA

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**Abstract**—Ceria (CeO<sub>2</sub>) is considered as one of materials for the simultaneous removal of SO<sub>2</sub> and NO<sub>x</sub> from flue gas. Ceria was coated on honeycomb and tested for adsorption of SO<sub>2</sub> and reduction of NO with ammonia. Experimental results showed the characteristics similar to copper oxide but reactivity for NO reduction was higher in broader temperature range compared with the latter.

### INTRODUCTION

With increasing use of fossil fuel air pollution is becoming a serious problem in this country. SO<sub>x</sub> and NO<sub>x</sub>, which air formed when fossil fuel burns, are known as major precursors of acid rain and thus abatement of their emission is a major target in air pollution control. Accordingly many different processes have been developed for the removal of SO<sub>x</sub> and NO<sub>x</sub> from flue gas [1]. For the removal of SO<sub>x</sub> limestone slurry process producing gypsum as a byproduct is widely employed, while selective catalytic reduction (SCR) is usually opted for the removal of NO<sub>x</sub>. Thus for the removal of both SO<sub>x</sub> and NO<sub>x</sub> these two processes should be used in series.

However, those two processes are based on entirely different principles and chemistry, thus implementation of them incurs rather high cost. In order to simplify and thus reduce the cost associated with deSO<sub>x</sub> and deNO<sub>x</sub> of flue gas, processes for simultaneous removal of SO<sub>x</sub> and NO<sub>x</sub> have been developed. They include processes using active coke, copper oxide or ceria as an adsorbent for deSO<sub>x</sub> and SCR catalyst for deNO<sub>x</sub>. Electron beam process is also under development for the simultaneous removal of SO<sub>x</sub> and NO<sub>x</sub>. Concept of ceria process is schematically shown in Fig. 1. Ceria (CeO<sub>2</sub>) has been studied as additive in catalytic converter of automobiles or adsorbent of SO<sub>2</sub> in regenerator of FCC. However, only recent studies on simultaneous deSO<sub>x</sub> and deNO<sub>x</sub> are made. Ginger [2] obtained a patent on the method of simultaneous deSO<sub>x</sub> and deNO<sub>x</sub> using catalysts impregnated with

copper and cerium. He reported better adsorption of SO<sub>2</sub> with the addition of cerium compared with impregnation of copper. Longo [3] impregnated alumina with ceria and used it for the removal of SO<sub>2</sub> and NO<sub>x</sub> at 500-700°C. Bertolacini et al. [4] added to cracking catalyst a small amount of alumina impregnated with ceria, and performed SO<sub>2</sub> adsorption test with it.

Ceria impregnated alumina (CeO<sub>2</sub>/γ-Al<sub>2</sub>O<sub>3</sub>) has various merits. Ceria imparts thermal stability to alumina thus surface area of the latter does not decrease at high temperatures. Ceria can remove two moles of SO<sub>2</sub> per mole by forming Ce(SO<sub>4</sub>)<sub>2</sub> with SO<sub>2</sub>, and reactivity is high in broad temperature range. Gases produced in regeneration are suitable for Claus process to be converted to elemental sulfur. For deNO<sub>x</sub> its role is similar to other SCR catalysts in reducing nitric oxide with ammonia.

In the treatment of flue gas minimization of pressure drop is very important for economical reasons. Therefore use of reactors with low pressure drop such as honeycomb is inevitable in practice. In this study we used simulated flue gas and honeycomb impregnated with ceria for the investigation of deSO<sub>x</sub> and deNO<sub>x</sub> characteristics of ceria.

### EXPERIMENT

#### 1. Preparation of Sorbent/Catalyst

200 gram of alumina (United Catalysts Inc. CS-331-4 γ-Al<sub>2</sub>O<sub>3</sub>) was put into 300 cc of distilled water and pulverized in a planetary mill at 130 rpm. After 5 hours of milling mean size of alumina particles was reduced to 1.66 μm. Aluminum nitrate was added to this slurry as gluing agent and well stirred. Then a

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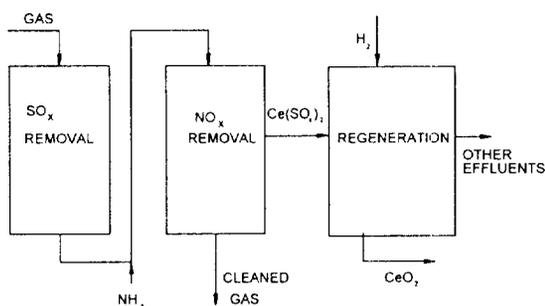


Fig. 1. Scheme for simultaneous removal of  $\text{SO}_2$  and  $\text{NO}_x$ .

predetermined amount of cerium nitrate was added and well mixed. Honeycomb (Product of Dongseo Ind. Co.) employed in this study was made of cordierite with 400 CPSI (Cells Per Square Inch). Its diameter was 10 mm and length 40 mm. Honeycomb was without skin. Honeycomb was dipped into the slurry prepared as described in the above. After insuring all the cells plugged with slurry honeycomb was removed from the slurry and excess slurry was blown out from the honeycomb with the aid of compressed air. Care was taken to obtain uniform coating. After drying of surface in the air honeycomb was put into a dry oven. After complete drying at  $100^\circ\text{C}$  it was calcined at  $650^\circ\text{C}$  for 2 hours. The procedure of sorbent/catalyst pre-

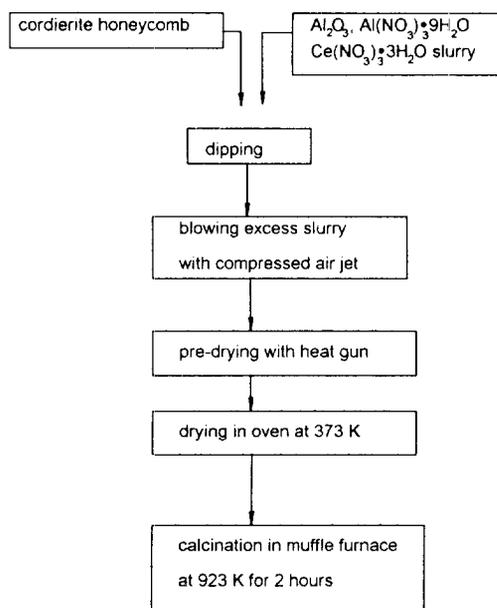


Fig. 2. Schematic diagram of honeycomb sorbent/catalyst preparation.

paration is summarized in Fig. 2.

## 2. Apparatus and Methods of Experiment

Experimental set-up for  $\text{SO}_2$  adsorption and  $\text{NO}_x$

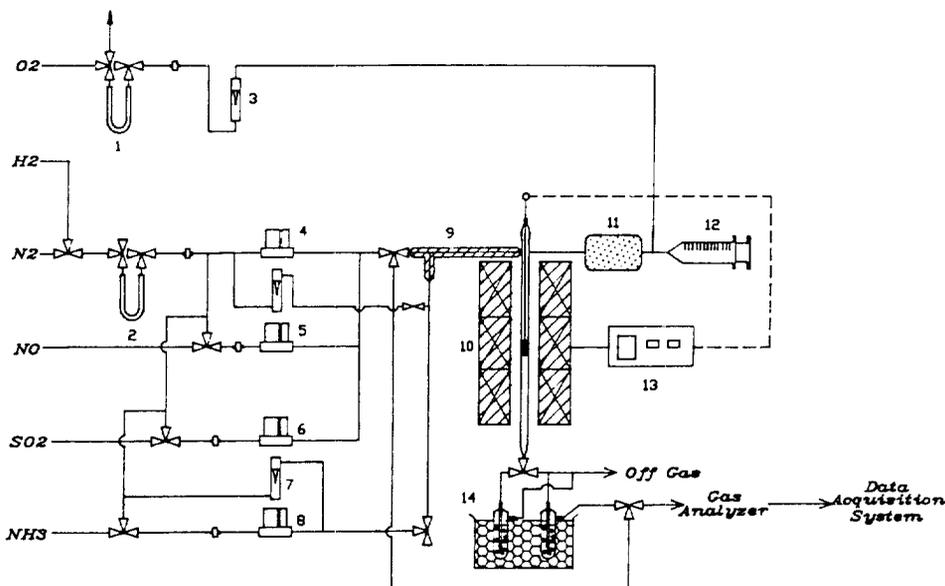


Fig. 3. Schematic flow diagram of reactor system.

1 & 2: oxygen/moisture trap, 3 & 7: rotameter, 4, 5, 6 & 8: mass flow controller, 9: preheater, 10: furnace, 11: steam generator, 12: syringe pump, 13: temperature controller, 14:  $\text{NH}_3$  trap.

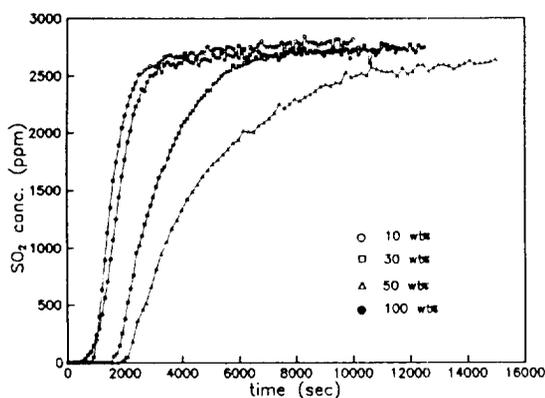


Fig. 4. Effect of CeO<sub>2</sub> contents in slurry on SO<sub>2</sub> adsorption.

temperature: 600°C, space velocity: 2830 hr<sup>-1</sup>, SO<sub>2</sub> concentration: 2800 ppm, O<sub>2</sub> concentration: 3%, H<sub>2</sub>O concentration: 5.4%.

reduction is schematically shown in Fig. 3. Sulfur dioxide, nitric oxide, oxygen, ammonia, and nitrogen gases were supplied from cylinders, and their flow rates were controlled with MFC (Unit Co.). Gas lines were kept at 200°C to prevent formation of salts such as NH<sub>4</sub>NO<sub>3</sub>, NH<sub>4</sub>NO<sub>2</sub>, and (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> through reaction of NH<sub>3</sub> with NO and SO<sub>2</sub>. Distilled water was fed through a syringe pump and then vaporized by passing through a tube maintained at 300°C. Feed gas line was branched into two. One of them is directly connected to the reactor while the other connected to gas analyzing system, so that feed gas composition could be measured before the beginning of an experimental run. Reactor was made of a quartz tube. Its diameter was 2 cm, length 61.5 cm. Honeycomb was put into the middle section of the reactor. Packing material was put in between the honeycomb and inside wall of the reactor to prevent gas bypassing. Effluent gas passed through an ice bath or water trap and boric acid solution to remove unreacted NH<sub>3</sub> before reaching gas analyzer (NDIR type, Horiba VIA-300) for the measurement of SO<sub>2</sub> and NO concentration.

## RESULTS AND DISCUSSION

### 1. Effects of Ceria Loading on SO<sub>2</sub> Adsorption

Preliminary tests showed that packing material did not adsorb steam and SO<sub>2</sub>. Weight fraction of ceria in the slurry was varied to study effects of ceria loading on SO<sub>2</sub> adsorption. The amount of slurry coated on honeycomb was about the same except for 100% ceria slurry. As shown in Fig. 4 breakthrough time

Table 1. Effect of CeO<sub>2</sub> contents in slurry on SO<sub>2</sub> adsorption

	10%	30%	50%	100%
The amount of slurry coating (wt%)	24.3	26.8	22.8	6.2
Weight of CeO <sub>2</sub> in slurry (gr)	0.208	0.710	0.984	0.539
t <sub>1</sub> * (sec) Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	814	2774	3846	2105
t <sub>2</sub> * (sec) Ce(SO <sub>4</sub> ) <sub>2</sub>	1086	3699	5128	2807
t <sub>250</sub> (sec)	1028	1900	2320	1000
t <sub>500</sub> (sec)	1144	2100	2735	1258
t <sub>250</sub> /t <sub>1</sub> *	1.26	0.68	0.60	0.47
t <sub>250</sub> /t <sub>2</sub> *	0.94	0.51	0.45	0.35
t <sub>500</sub> /t <sub>1</sub> *	1.40	0.75	0.71	0.59
t <sub>500</sub> /t <sub>2</sub> *	1.05	0.56	0.53	0.44

Note) SO<sub>2</sub> adsorption conditions are as in Fig. 4.

of SO<sub>2</sub> increased with ceria loading except for the case of 100% ceria coating. The exception in the Fig. 4 could be explained by the weight of CeO<sub>2</sub> in the Table 1. The breakthrough time of SO<sub>2</sub> adsorption is proportional to the weight of CeO<sub>2</sub> rather than that of content. The case of 100% coating in the Fig. 4 had a smaller ceria utilization efficiency which came from the poor ceria dispersity on the alumina. In Table 1 the above results were summarized. Here t\* denotes hypothetical time required for complete conversion of ceria honeycomb into sulfate with SO<sub>2</sub> in reactant gas assuming 100% consumption of SO<sub>2</sub> in the process. Subscript 1 and 2 denote sulfate form as Ce<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> and Ce(SO<sub>4</sub>)<sub>2</sub>, respectively [4]. t<sub>250</sub> and t<sub>500</sub> denote the elapse of time between injection of SO<sub>2</sub> and the moment when concentration of SO<sub>2</sub> reached 250 and 500 ppm, respectively. By comparing normalized breakthrough time in Table 1 we can notice utilization efficiency of ceria decreased with ceria loading. This is believed due to deterioration in dispersion of ceria with increasing loading. In the case of 10% ceria loading conversion of ceria to sulfate resulted in higher value than stoichiometry of CeO<sub>2</sub> to Ce(SO<sub>4</sub>)<sub>2</sub>. Similar behavior was observed for alumina pellets impregnated with ceria. This is an indication that alumina participated in adsorption of SO<sub>2</sub>.

### 2. Effects of Temperature

Adsorption of SO<sub>2</sub> at various temperatures is shown in Fig. 5. The amount of SO<sub>2</sub> adsorption increased as temperature was increased from 400°C to 600°C. At 700°C decrease of adsorption was observed for alumina pellets impregnated with ceria [6]. The comparison of SO<sub>2</sub> adsorption performance between copper oxide and ceria catalyst was shown in Table 2. The

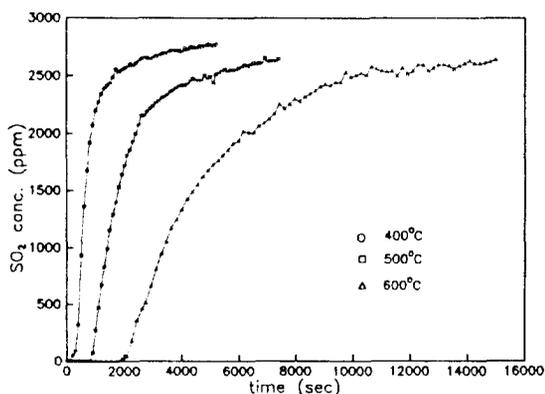


Fig. 5. Effect of temperature on  $\text{SO}_2$  adsorption.

space velocity:  $2830 \text{ hr}^{-1}$ ,  $\text{SO}_2$  concentration: 2900 ppm,  $\text{O}_2$  concentration: 3%;  $\text{H}_2\text{O}$  concentration: 5.4%.

Table 2. Comparison of  $\text{SO}_2$  adsorption capacity between ceria and copper oxide

Temperature (°C)	$\text{CeO}_2$		$\text{CuO}$		Weight content of catalysts (g)	
	$t_{250}$	$t_{500}$	$t_{250}$	$t_{500}$	$\text{CeO}_2$	$\text{CuO}$
400	280	929	552	667	0.974	1.0495
500	980	1110	1337	1515	0.971	1.001
600	2320	2735	931	1200	0.984	0.918

weight of copper oxide and ceria used in experiments were almost the same in order to make equivalent amount of  $\text{SO}_2$  adsorption per mole of catalyst. As shown in Table 2, the better  $\text{SO}_2$  adsorption performance was observed in copper oxide in the range of 400-500°C while ceria showed higher performance at 600°C.

### 3. Effects of Space Velocity

Table 3 shows the effect of space velocity on the  $t_{250}$ ,  $t_{500}$  and their normalized values by  $t_1^*$ . When space velocity decreased from 8488/hr to 2840/hr breakthrough time increased about five folds and utilization efficiency, represented as  $t_{250}/t_1^*$  and  $t_{500}/t_1^*$ , increased by two folds.

### 4. DeNO<sub>x</sub> Characteristics

Reduction of NO with ammonia over ceria impregnated honeycomb was also studied. Composition of reactant gases was NO of 1,000 ppm,  $\text{NH}_3$  of 1,000 ppm,  $\text{O}_2$  of 3%, and  $\text{H}_2\text{O}$  of 5.4%. The balance was nitrogen. Volumetric gas flow rate was set to 1 liter per minute. Space velocity based on honeycomb volume was 2830/hr. With 50% ceria slurry the amount coated on honeycomb was 24% of honeycomb weight.

Table 3. Effect of space velocity on  $\text{SO}_2$  adsorption

S.V. ( $\text{hr}^{-1}$ )	$t_{250}$ (sec)	$t_{500}$ (sec)	$t_{250}/t_1^*$	$t_{500}/t_1^*$	Coating $\text{CeO}_2$	
					amount (%)	amount (gr)
8488	190	210	0.6397	0.707	26.7	0.0761
2830	1028.5	1144	1.263	1.405	24.3	0.2085

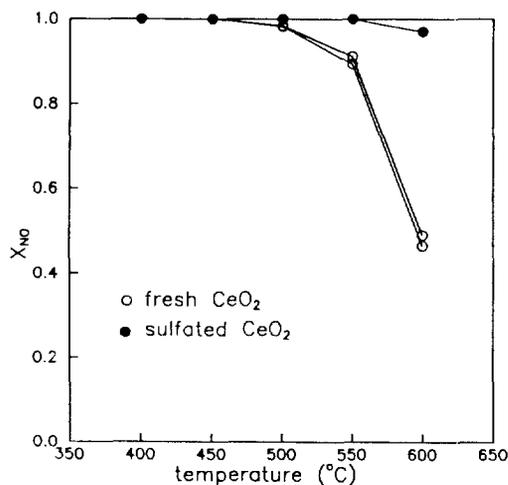


Fig. 6. Effect of temperature on NO conversion and reproductibility for  $\text{CeO}_2$  washcoated honeycomb.

The NO reduction efficiency of the ceria wash-coated honeycomb is shown in Fig. 6. The ceria showed high efficiency (>90%) below 500°C. However, NO reduction efficiency of ceria decreased with increasing temperature. At 600°C, the conversion of NO over the ceria catalyst less than 50%. The decrease in NO conversion with increasing temperature was due to ammonia oxidation on the sorbent-catalysts at higher temperature.

The effect of partial sulfation of ceria on the NO reduction efficiency is also shown in Fig. 6. For the test, the ceria sorbent was sulfated in 3000 ppm  $\text{SO}_2$  flow. The comparison of the NO reduction effectiveness of partially sulfated ceria with fresh one clearly shows that the former has high SCR reactivity. The  $\text{NO}_x$  reduction behavior on partially sulfated ceria was not revealed in the literature [7]. Therefore, further works will be needed to find the relationship between the fresh and partially sulfated ceria catalyst.

## CONCLUSIONS

In this study we investigated experimentally the potential of ceria for the simultaneous removal of  $\text{SO}_2$

and NO<sub>x</sub> from flue gas. Experimental results showed that ceria could be satisfactorily coated on honeycomb. Tests for SO<sub>x</sub> adsorption exhibited general trend common to metal oxide such as copper oxide. However, more studies are needed for better utilization of sorbent. For deNO<sub>x</sub>, ceria showed good reactivity at broader temperature range compared to copper oxide.

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