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REMOVAL OF SO_x AND NO_x FROM FLUE GAS WITH CERIA

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Abstract—Ceria (CeO_2) is considered as one of materials for the simultaneous removal of SO_x and NO_x from flue gas. Ceria was coated on honeycomb and tested for adsorption of SO_2 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_x and NO_x, 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_x and NO_x from flue gas [1]. For the removal of SO_x limestone slurry process producing gypsum as a byproduct is widely employed, while selective catalytic reduction (SCR) is usually opted for the removal of NO_x. Thus for the removal of both SO_x and NO_x 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_x and deNO_x of flue gas, processes for simultaneous removal of SO_x and NO_x have been developed. They include processes using active coke, copper oxide or ceria as an adsorbent for deSO_x and SCR catalyst for deNO_x. Electron beam process is also under development for the simultaneous removal of SO_x and NO_x. Concept of ceria process is schematically shown in Fig. 1. Ceria (CeO_2) has been studied as additive in catalytic converter of automobiles or adsorbent of SO_2 in regenerator of FCC. However, only recent studies on simultaneous deSO_x and deNO_x are made. Ginger [2] obtained a patent on the method of simultaneous deSO_x and deNO_x using catalysts impregnated with copper and cerium. He reported better adsorption of SO_2 with the addition of cerium compared with impregnation of copper. Longo [3] impregnated alumina with ceria and used it for the removal of SO_2 and NO_x at 500-700℃. Bertolacini et al. [4] added to cracking catalyst a small amount of alumina impregnated with ceria, and performed SO_2 adsorption test with it.

Ceria impregnated alumina (CeO_2/γ-Al_2O_3) 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_2 per mole by forming $Ce(SO_4)_2$ with SO_2, 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_x 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_x and deNO_x characteristics of ceria.

EXPERIMENT

1. Preparation of Sorbent/Catalyst

200 gram of alumina (United Catalysts Inc. CS-331-4 γ-Al_2O_3) 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 mm. Aluminum nitrate was added to this slurry as gluing agent and well stirred. Then a

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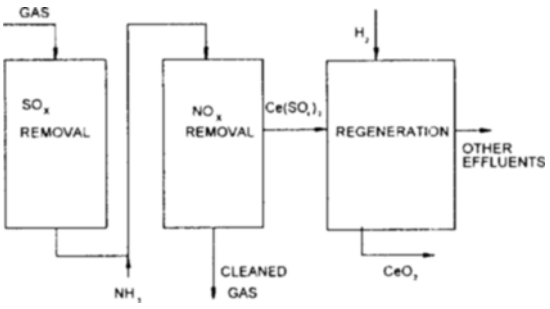

Fig. 1. Scheme for simultaneous removal of SO_2 and NO_x.

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 100C it was calcined at 650 C for 2 hours. The procedure of sorbent/catalyst preparation is summarized in Fig. 2.

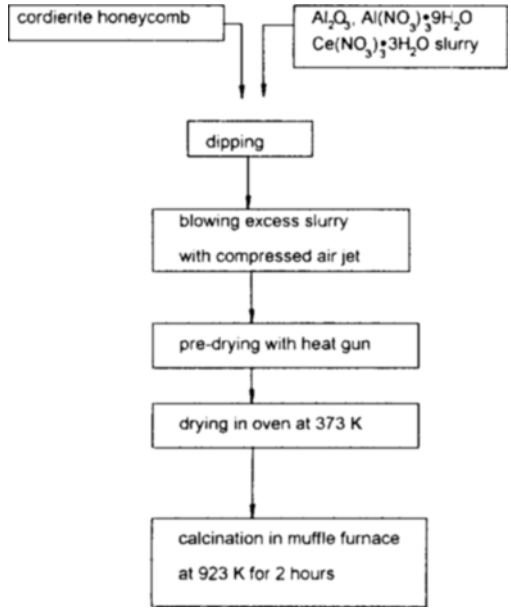

Fig. 2. Schematic diagram of honeycomb sorbent/catalyst preparation.

2. Apparatus and Methods of Experiment

Experimental set-up for SO_2 adsorption and NO_x

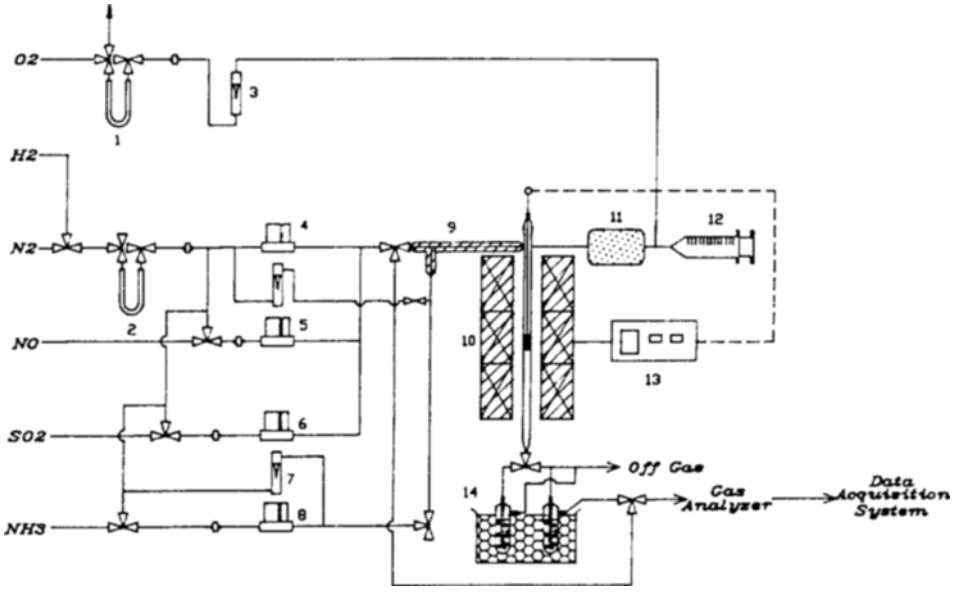

Fig. 3. Schematic flow diagram of reactor system.

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: NH_3 trap.

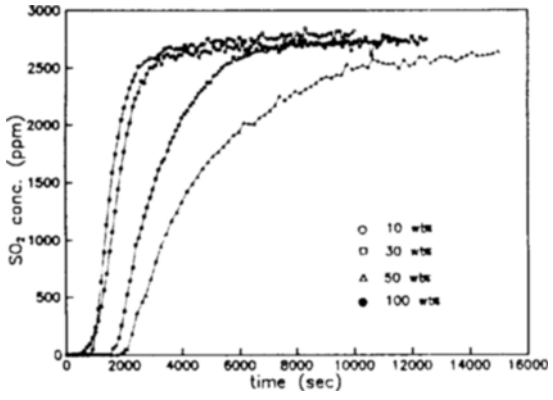

Fig. 4. Effect of CeO_2 contents in slurry on SO_2 adsorption.

temperature: 600℃, space velocity: 2830 hr^{-1}, SO_2 concentration: 2800 ppm, O_2 concentration: 3%, H_2O concentration: 5.4%.

reduction is schematically shown in Fig. 3. Sulfur dioxide, nitric oxide, oxygen, ammonia, and nitrogen gases were supplied from cyclinders, and their flow rates were controlled with MFC (Unit Co.). Gas lines were kept at 200℃ to prevent formation of salts such as NH_4NO_3, NH_4NO_2, and $(NH_4)_2SO_4$ through reaction of NH_3 with NO and SO_2. Distilled water was fed through a syringe pump and then vaporized by passing through a tube maintained at 300℃. 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_3 before reaching gas analyzer (NDIR type, Horiba VIA-300) for the measurement of SO_2 and NO concentration.

RESULTS AND DISCUSSION

1. Effects of Ceria Loading on SO_2 Adsorption

Preliminary tests showed that packing material did not adsorb steam and SO_2. Weight fraction of ceria in the slurry was varied to study effects of ceria loading on SO_2 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_2 contents in slurry on SO_2 adsorption

	10%	30%	50%	100%
The amount of slurry coating (wt%)	24.3	26.8	22.8	6.2
Weight of CeO_2 in slurry (gr)	0.208	0.710	0.984	0.539
t_1* (sec) $Ce_2(SO_4)_3$	814	2774	3846	2105
t_2* (sec) $Ce_2(SO_4)_2$	1086	3699	5128	2807
t_{250} (sec)	1028	1900	2320	1000
t_{500} (sec)	1144	2100	2735	1258
t_{250}/t_1*	1.26	0.68	0.60	0.47
t_{250}/t_2*	0.94	0.51	0.45	0.35
t_{500}/t_1*	1.40	0.75	0.71	0.59
t_{500}/t_2*	1.05	0.56	0.53	0.44

Note) SO_2 adsorption conditions are as in Fig. 4.

of SO_2 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_2 in the Table 1. The breakthrough time of SO_2 adsorption is proportional to the weight of CeO_2 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_2 in reactant gas assuming 100% consumption of SO_2 in the process. Subscript 1 and 2 denote sulfate form as $Ce_2(SO_4)_3$ and $Ce(SO_4)_2$, respectively [4]. t_{250} and t_{500} denote the elapse of time between injection of SO_2 and the moment when concentration of SO_2 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_2 to $Ce(SO_4)_2$. Similar behavior was observed for alumina pellets impregnated with ceria. This is an indication that alumina participated in adsorption of SO_2.

2. Effects of Temperature

Adsorption of SO_2 at various temperatures is shown in Fig. 5. The amount of SO_2 adsorption increased as temperature was increased from 400℃ to 600℃. At 700℃ decrease of adsorption was observed for alumina pellets impregnated with ceria [6]. The comparison of SO_2 adsorption performance between copper oxide and ceria catalyst was shown in Table 2. The

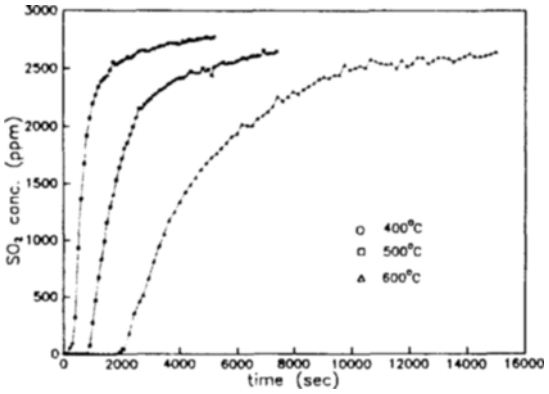

Fig. 5. Effect of temperature on SO_2 adsorption.
space velocity: 2830 hr^{-1}, SO_2 concentration: 2900 ppm, O_2 concentration: 3%; H_2O concentration; 5.4 %.

Table 2. Comparison of SO_2 adsorption capacity between ceria and copper oxide

Temperature (℃)	CeO_2		CuO		Weight content of catalysts (g)	
	t_{250}	t_{500}	t_{250}	t_{500}	CeO_2	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 SO_2 adsorption per mole of catalyst. As shown in Table 2, the better SO_2 adsorption performance was observed in copper oxide in the range of 400-500℃ while ceria showed higher performance at 600℃.

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$_x$ Characteristics

Reduction of NO with ammonia over ceria impregnated honeycomb was also studied. Composition of reactant gases was NO of 1,000 ppm, NH_3 of 1,000 ppm, O_2 of 3%, and H_2O 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 SO_2 adsorption

S.V (hr^{-1})	t_{250} (sec)	t_{500} (sec)	t_{250}/t_1*	t_{500}/t_1*	Coating amount (%)	CeO_2 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

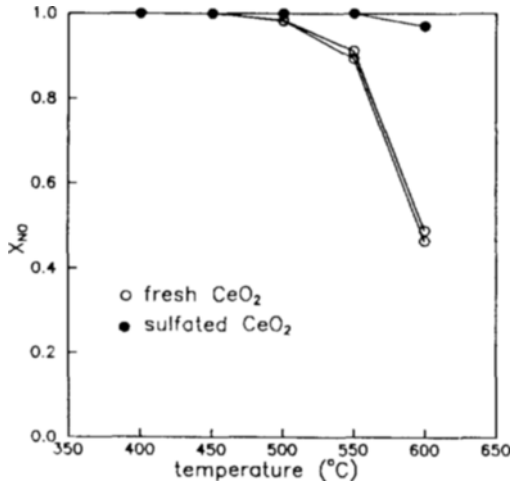

Fig. 6. Effect of temperature on NO conversion and reproducibility for CeO_2 washcoated honeycomb.

The NO reduction efficiency of the ceria wash-coated honeycomb is shown in Fig. 6. The ceria showed high efficiency (>90%) below 500℃. However, NO reduction efficiency of ceria decreased with increasing temperature. At 600℃, 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 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 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 SO_x

and NO_x from flue gas. Experimental results showed that ceria could be satisfactorily coated on honetcomb. Tests for SO_x adsorption exhibited general trend common to metal oxide such as copper oxide. However, more studies are needed for better utilization of sorbent. For deNO_x ceria showed good reactivity at broader temperature range compared to copper oxide.

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