

## Study of Catalytic Ceramic Fiber Filter Elements for Hot Gas Filtration

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CuO catalyst-coated alumino-silicate fiber filters were prepared for the simultaneous removal of particulate matter and gaseous contaminants such as NO<sub>x</sub> and SO<sub>x</sub>. Hot gas cleaning experiments similar to Shell UOP process other than the catalyst supporting materials were carried out between 300 and 500°C for the evaluation of the gas removal efficiency of the catalytic filter. Experimental results showed that removal efficiency for SO<sub>2</sub> was greater than 99% in the temperature range 450 ~ 500°C and more than 90% of NO was collected between 350 and 370°C. It was found that the higher the CuO content, the higher the removal efficiency for SO<sub>2</sub>. Removal efficiency for NO was more affected by the gas cleaning temperature than by the CuO content in the catalyst-coated filter.

**Key words** : Hot gas cleaning, Ceramic fiber, Catalytic filter, SO<sub>x</sub>, NO<sub>x</sub>

### I. Introduction

Ceramic filter and ceramic catalyst support are the typical examples of practical applications of porous structure of heat resistant ceramics. Monolithic ceramic filters have been used for an element in the high temperature dust removal systems in the various fields of industry.<sup>1,2)</sup> Ceramics of high specific surface area such as silica, alumina and zeolite are widely applied in exhaust gas catalysis.<sup>3)</sup> In the literature, catalytic filter is known as an element which can simultaneously remove particulate matter and gaseous contaminants such as oxides of nitrogen and sulfur dioxide.<sup>4)</sup> One advantage of the catalytic filter is that two processes can be achieved in a single device. In the above instance, the processes are particulate removal and catalytic reduction of gaseous contaminants.

In this study we report the gas cleaning efficiency of catalytic ceramic filters in which CuO catalyst is coated on alumino-silicate fiber. Effects of CuO catalyst loading and gas cleaning temperature on the removal efficiency for SO<sub>2</sub> and NO were discussed. The gas removal process was similar to Shell UOP process other than the catalyst supporting material. The Shell UOP process which utilizes ceramic honeycomb monoliths is well known for its high removal efficiency for SO<sub>x</sub> and NO<sub>x</sub>.<sup>5)</sup>

### II. Experimental Procedure

#### 1. Preparation and characterization of catalytic ceramic fiber filters

Catalytic ceramic fiber filter elements with porosity in the range of 82-86% were prepared in this study. Disc

shaped samples, 50 mm in diameter and 10 mm thick, were vacuum molded from a slurry mixture of alumino-silicate fiber, and organic and inorganic binders, e.g., colloidal alumino-silicates and starch. The washcoating of the filter sample was carried out simultaneously by the dipping method. The filter sample was dipped into the colloidal alumino-silicate sol. The washcoated sample after drying was calcined at 600°C for one hour. The obtained ceramic fiber filter samples had the average porosity of about 87%. Aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O were used to load copper by the adsorption method on the filter samples. Concentration of copper nitrate solution was

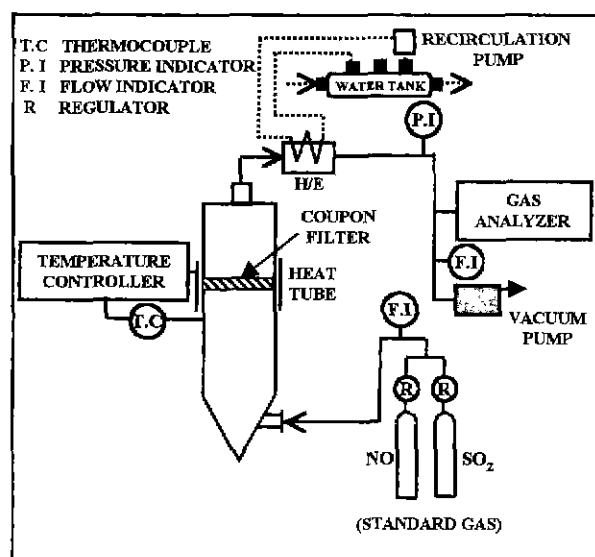


Fig. 1. Schematic diagram of experimental set-up.

adjusted for appropriate copper loading, i.e., 5, 10, 15, 20, and 30 wt% CuO. After drying followed by calcination of the copper loaded samples at 600°C in flowing air, CuO catalyst-coated ceramic fiber filter samples were obtained.

The structure of the catalyst filter samples was studied by X-ray diffractometry with Cu K $\alpha$  monochromatic radiation. The surface areas and pore size distributions of the samples were determined by multi-point BET and BJH method using nitrogen desorption isotherms, respectively. The microstructure of the samples was examined by scanning electron microscopy.

## 2. Experimental set-up for simultaneous removal of SO<sub>2</sub> and NO

A schematic diagram of the experimental set-up is shown in Fig.1. The main gas stream supplied by a standard gas tank (SO<sub>2</sub>: 2,500 PPM, NO: 1480 ppm) and catalytic filter sample are electrically heated up to 600°C using

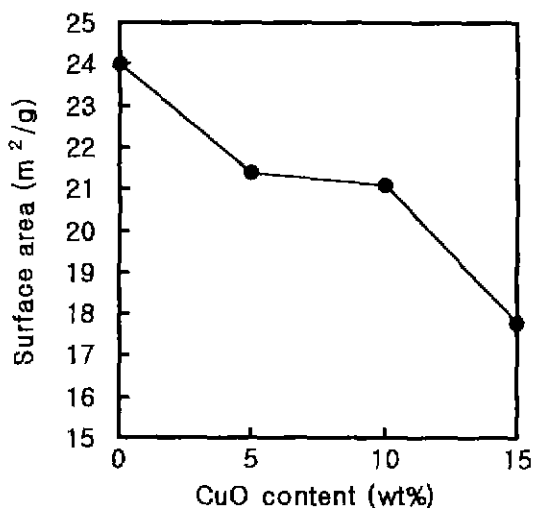


Fig. 2. Effect of CuO content on the specific surface area of catalytic filter.

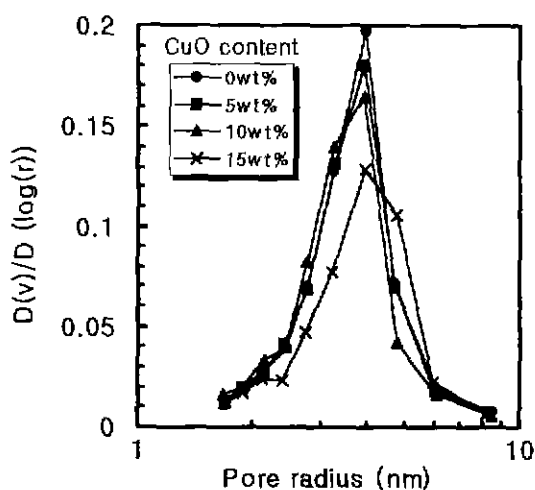


Fig. 3. The pore size distribution of catalytic filters with different CuO content.

a heat tube. A gas analyzing system (IMR 3000P) installed at the end of the gas outlet was used for continuous monitoring of flowing gas to evaluate the removal efficiency of the catalytic filter.

## III. Results and Discussion

### 1. Properties of catalytic filters

Specific surface area (SSA) of the filter sample was about 24 m<sup>2</sup>g<sup>-1</sup>. Fig. 2 shows the effect of CuO loading on the SSA of the catalyst support. The SSA decreased with increasing CuO content. In general SSA of oxide catalyst support such as gamma alumina decreases with increasing catalyst loading.<sup>6</sup> The decrease in the SSA was attributed to the plugging of some mesopores of the support by the catalyst.

The pore size distribution of the catalyst support is shown in Fig. 3. All the catalyst support with different CuO contents had the dominant pore diameter about

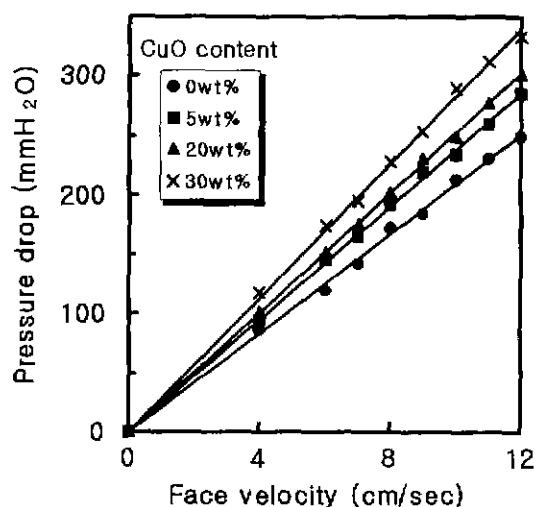


Fig. 4. Pressure drop of catalytic filter element as a function of face velocity.

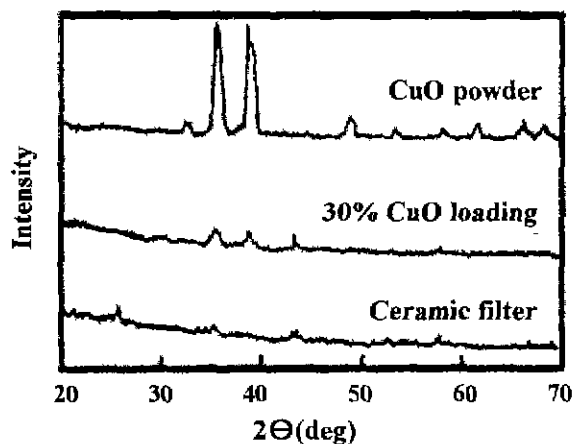


Fig. 5. XRD patterns of (a) CuO powder, (b) non-catalytic filter sample and (c) catalytic filter sample with 30% CuO.

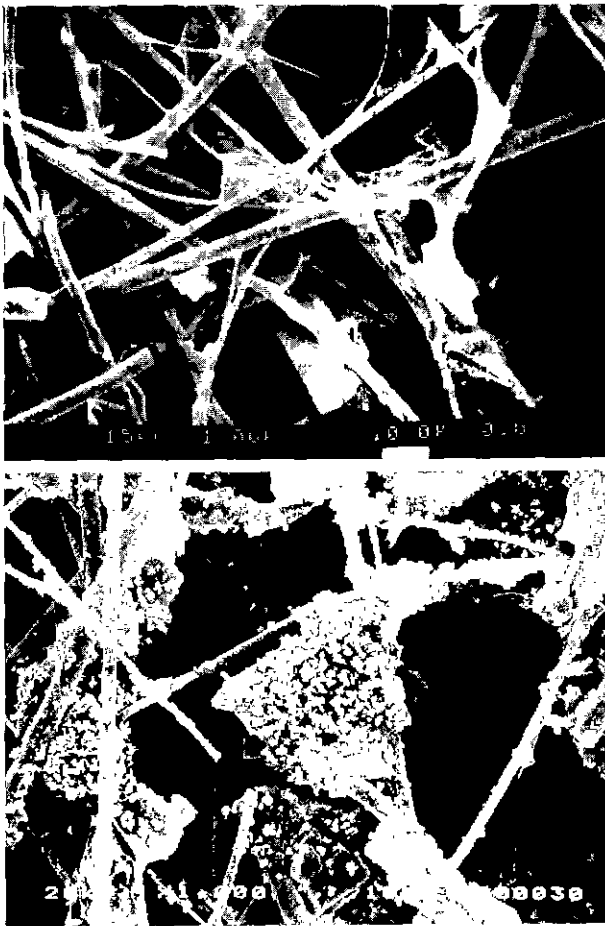


Fig. 6. Micrographs of (a) non-catalytic filter sample and (b) catalytic filter sample.

8 nm. This value is similar to the that of  $\gamma$ -alumina calcined at 600°C.<sup>71</sup>

It is important to characterize changes in gas permeability of gas filter caused by catalyst loading. Fig. 4

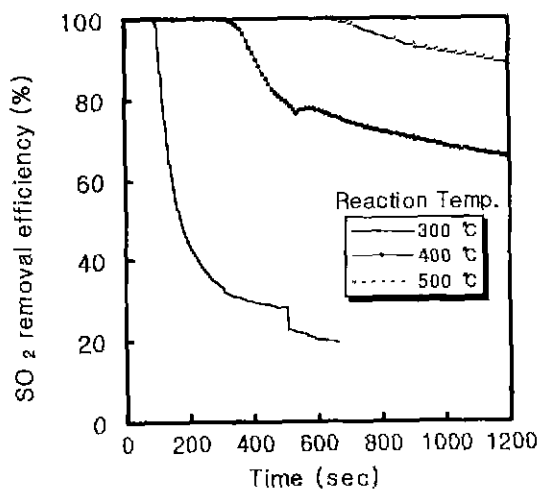


Fig. 7. Time dependent removal efficiency for  $\text{SO}_2$  at different gas cleaning temperatures.

shows the effect of  $\text{CuO}$  content on the pressure drop as a function of face velocity for filter samples. As can be seen, the non-catalytic sample shows the lowest pressure drop. The value for the catalytic samples loaded with  $\text{CuO}$  was always higher than that for the non-catalytic sample for all face velocities. This difference in pressure drop between these samples was due to the washcoating material and the excess copper loading which leads to form bulk  $\text{CuO}$  crystallites on the surface of catalyst support. The colors of the catalytic sample coincide with those known in the literature.<sup>61</sup> When the dark or black color was observed, the bulk copper oxide was formed as confirmed by XRD analysis and microstructural study of the catalytic samples.

In Fig. 5, XRD patterns of  $\text{CuO}$  powder, and non-catalytic and catalytic filter samples are compared. Two small peaks at  $2\theta=35.6^\circ$  and  $38.7^\circ$  shown in Fig. 5 are contributed by bulk  $\text{CuO}$  crystallites formed on the catalytic fil-

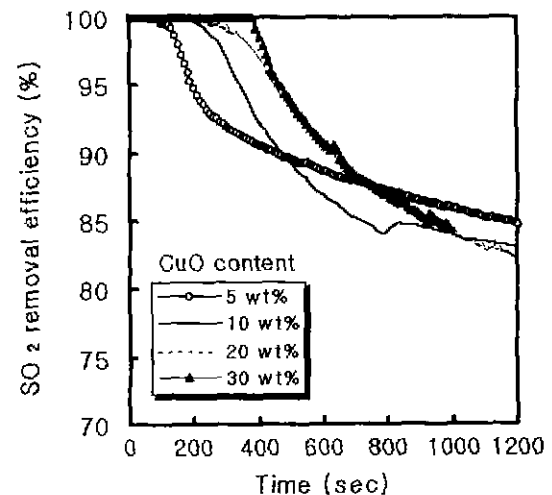


Fig. 8. Time dependent removal efficiency for  $\text{SO}_2$  at different  $\text{CuO}$  content of catalytic filters.

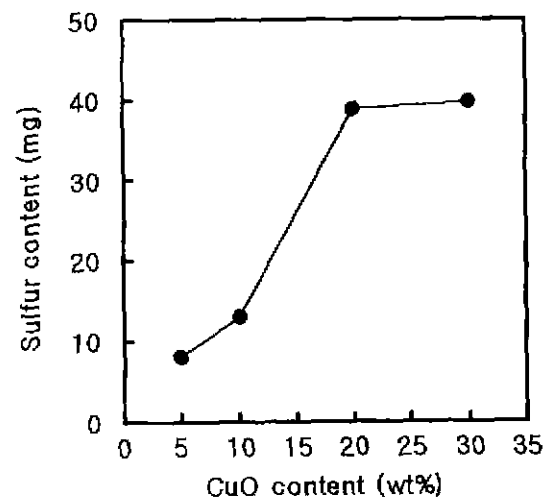


Fig. 9. Sulfur content retained in catalytic filters after reaction as a function of  $\text{CuO}$  content.

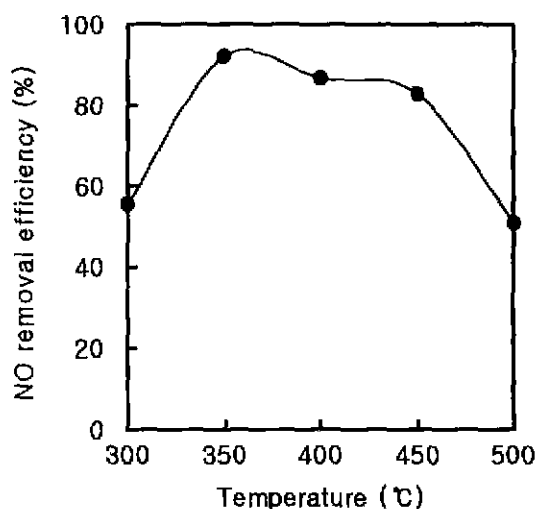


Fig. 10. Removal efficiency for NO at different gas cleaning temperatures.

ter. Micrographs of non-catalytic and catalytic filter sample are shown in Fig. 6. As seen from this figure, precipitated CuO particles are scattered on the surface of the washcoating materials.

## 2. Removal efficiency for SO<sub>2</sub> and NO

Effects of reaction temperature and CuO content on removal efficiency for SO<sub>2</sub> was investigated. Fig. 7 shows the results for the removal efficiency obtained with the 15% CuO-containing catalytic filter. The removal efficiency increased with increasing the reaction temperature. There was an initial time period in which removal efficiency greater than 99% was achieved. At a higher temperature this time period was extended and was about 10 minutes at 500°C. With the lowering the reaction temperature, the removal efficiency decreased more rapidly with a steeper slope as shown in Fig. 7. It is considered that the initial high removal efficiency results from the distinct microstructure of the monolithic catalytic filter element which can be characterized by porosity higher than 80% and a large exchange surface, which enables efficient mass transfer between CuO particles and SO<sub>2</sub> gas.

Fig. 8 shows the effects of CuO content between 5 and 30 wt% on removal efficiency of SO<sub>2</sub> at 500°C. The time periods in which removal efficiency remains values of more than 99% increased to 100, 200, 220, and 380 sec for CuO content of 5, 10, 20, and 30 wt%, respectively. The increase of CuO content led to an increase in the sulfur content of catalytic filter sample after reaction as shown in Fig. 9.

Fig. 10 shows the removal efficiency for NO as a func-

tion of gas cleaning temperature. When the feeding of the ammonia equimolar to the NO concentration, the removal efficiencies of more than 80% were achieved in the temperature range 350~450°C. Considering that the SCR process for NO<sub>x</sub> removal commonly works in the temperature range 300~400°C, the present gas cleaning process requires operating temperature higher than SCR process in order to reach the maximum efficiency.

## IV. Conclusions

Ceramic fiber filter was used to prepare CuO catalyst-coated filter for the simultaneous removal of flue gas with solid particles. It was found that the amount of CuO loading had a significant effect on the pressure drop of the catalytic filter element due to the formation of bulk CuO crystallites in the support. Removal efficiency for SO<sub>2</sub> increased with CuO content, and was greater than 99% in the temperature range 450~500°C. Removal efficiency for NO was more than 90% in the temperature range 350~370°C and was more affected by the gas cleaning temperature than by CuO content in the catalytic filter.

## Acknowledgments

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