

Thermal and chemical degradation behavior of a catalytic ceramic filter for dust/NO_x removal

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The thermal and the chemical degradation characteristics of a catalytic ceramic filter were investigated using various stresses. The stress factors with modes and levels were designed in consideration of the pseudo-real environmental conditions for hot gas cleaning. The apparent porosity and the compressive strength of the filters, which were prepared using cordierite powder and coated with V₂O₅ catalyst were 58% and 10 MPa, respectively. The failure mechanism of the ceramic filter was cracking due to thermal shock. The crack formation gave an increase in baseline differential pressure by the depth filtration of dust. With thermal stress tests of catalytic filters, the peak intensity for active sites of the V₂O₅ catalyst was decreased due to the weak bond strength of the V=O double bond against the thermal stress. Moreover the degradation of the catalyst was accelerated by sulfur adsorption during thermal durability tests.

Key words: Catalytic ceramic filter, Durability, Thermal degradation, Chemical degradation, Hot gas cleaning.

Introduction

Ceramic filter elements and oxide catalyst carriers are typical examples of practical applications of heat resistant ceramics. Monolithic ceramic filters have been used for hot gas cleaning and dust removal in various industries. In the literature, a catalytic ceramic filter is known as an element which can simultaneously remove particulate matter and gaseous contaminants such as NO_x and VOCs [1]. One advantage of a catalytic filter is that two processes, particulate removal and catalytic reduction of gaseous contaminants, can be achieved in a single device [2]. On the other hand, the filters undergo thermo-mechanical constraints in the operating process, which may induce a reduction of catalyst efficiency and filter durability. Thermal or mechanical shock generated in the back-pulsing process separates the filtration layer from the filter or brings about cracking of the filter [3-6]. Also the activity of the de-NO_x catalyst decreases with time on stream depending on the operating conditions and the characteristics of the flue gas it is exposed to [7, 8]. The major causes of catalyst deactivation which have been reported in the technical literature are [7, 9]: (i) loss of surface area for sintering, (ii) poisoning of the flue gas in oil firing, (iii) plugging of catalyst pores by calcium compounds in coal firing, etc.

In the present study, thermal and chemical degradation

behavior of a catalytic filter was systematically investigated to find out the major cause of catalytic filter degradation. The degradation behavior of a catalytic filter was discussed through the changes of the pressure drop and NO_x removal efficiency of the degraded catalytic filter. Structural, morphological and chemical changes caused by thermal and chemical effects were observed.

Experimental Procedure

Ceramic filters were prepared by a pressing method using mixtures of cordierite powder, organic additives and a foaming agent. The specimens were dried at room temperature and at 100 °C for 24 h. The dried specimens were sintered at 1,410 °C. A filtration layer was deposited by a spray coating method on the support to prevent the fine powders from penetrating into the support.

The starting material for the coating of V₂O₅ for the de-NO_x catalyst was ammonium vanadate (Junsei Chemical Co., Ltd). Because this material is insoluble in water, oxalic acid (Duksan Pure Chemical Co., Ltd) was used to dissolve it. A vacuum dip coating system was designed to make the catalytic filter because it is impossible to coat catalyst inside the micro pores of the filter element with a conventional dip coating method. Samples were coated in solution for 30 minutes at a pressure lower than 0.133 Pa and dried at constant temperature and humidity. Then they were calcined at 600 °C for 1 h to activate the catalyst.

The intrinsic characteristics of filter elements such as apparent porosity and mechanical strength were measured

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Table 1. Properties of ceramic filter

Material	Porosity (%)	Strength (MPa)	Pore size (μm)	Pressure drop (Pa)
Cordierite	58	10	Support: 40-50 μm Filtration layer: < 1 μm	< 1300 (face velocity: 5 cm/s, 400 °C)

by a mercury porosimeter and universal testing machine (UTM), respectively. The pressure drop was estimated with the change of the face velocity and temperature.

In an attempt to examine the effect of thermal shock, thermal shock tests were performed by heating the filters to 325, 425, 525, and 625 °C, and then immersing them immediately in a cooling vessel at 25 °C to investigate the degradation behavior of filters. This thermal shock test was repeated 30, 50, 70, and 200 times. To study the chemical degradation behavior of the catalyst, the specimens were heated at temperature ranging from 450-600 °C for 200 h in air and in 600 ppm of SO_x. As the aim of the tests was to accelerate the formation of possible damage, the testing conditions were considerably stronger than those in normal operation.

The structural, morphological and chemical changes caused by thermal and chemical effects were observed by a field-emission scanning electron microscope (FE-SEM), X-ray diffractometry (XRD), X-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FT-IR), and the activity in the reduction of NO with ammonia.

Results and Discussion

Properties of catalytic filter

The porosity, the mechanical strength and the pressure drop of a filter influence the characteristics of the filter system such as the removal efficiency of dust and hazardous gases and the operating conditions. Therefore, a high porosity, a high mechanical strength and good permeability are needed to perform well for hot gas cleaning. Table 1 shows the properties of the filters prepared in this study. These filters

exhibited a porosity of 58%, a mechanical strength of 10 MPa and a pressure drop of 1,200 Pa at a face velocity of 5 cm/s and 400 °C. As the temperature was increased from room temperature to 400 °C, the pressure drop increased. This phenomenon is well known as the temperature dependency of the gas viscosity in Darcy's law. The pressure drop increases with temperature because the viscosity of the gas increases with temperature [10]. Nevertheless, these values are sufficient to apply the filters for the removal of a hazardous gas in an incineration system, etc.

Degradation behavior of ceramic filter

The effect of thermal shock and pressure shock on the durability of filter medium was observed. Generally, either too strong a cleaning pulse or degradation of the filter due to repeated cold cleaning pulses are considered to be the most influential reasons for failures of filters. But the pressure shock generated by a strong cleaning pulse did not damage the filter. After the pressure shock test, the strength of filter did not change and there were no cracks on the surface and inside the filter. Fig. 1 shows the variation of pressure drop after thermal shock tests at $T = 600$ °C. At $T = 300$ °C, a variation of pressure drop was not found and the pressure drop slightly decreased at $T = 400$ °C and 500 °C in the tests. However, the pressure drop was abruptly decreased as the number of repeated shock was increased at $T = 600$ °C. This result is attributed to the cracks formed at the surface or inside the filter by thermal shock as shown Fig. 2.

Fig. 2 illustrates the microstructure of filters after thermal shock tests at $T = 500$ °C. When we repeated the thermal shock test 50 times (Fig. 2(a)), cracks were generated on the surface of filter. Crack growth progressed as the number of repeated shocks increased (Fig. 2(b)). However, delamination was not observed between the support and filtration layer. If a crack was generated at the surface of the filter in normal conditions, depth filtration would be caused and it would bring about an increase in the baseline differential pressure and reduce the durability of filter.

Degradation behavior of catalyst

Thermal and chemical durability tests were performed to observe the degradation behavior of catalyst. The efficiency of catalysts in the reduction of NO by ammonia, which were heated at temperatures ranging from 450-600 °C for 200 h in air and 600 ppm of SO_x, are shown in Fig. 3. In the thermal durability tests (Fig. 3(a)), there was no variation of efficiency up to the aging temperature of 450 °C. From 500 °C, a decrease of efficiency was initiated

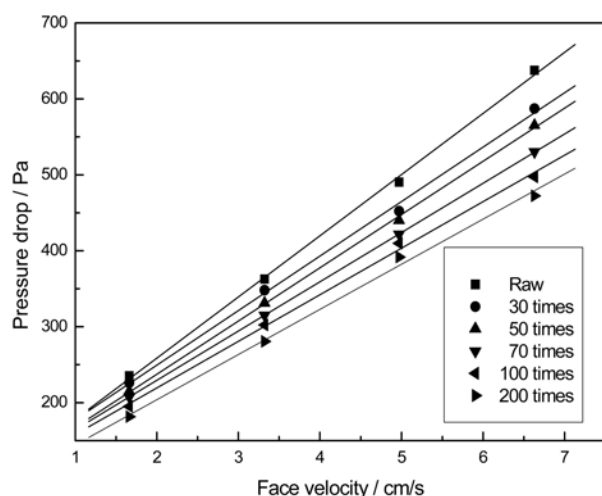


Fig. 1. Variation of pressure drop of filter after thermal shock cyclic tests at $T = 600$ °C.

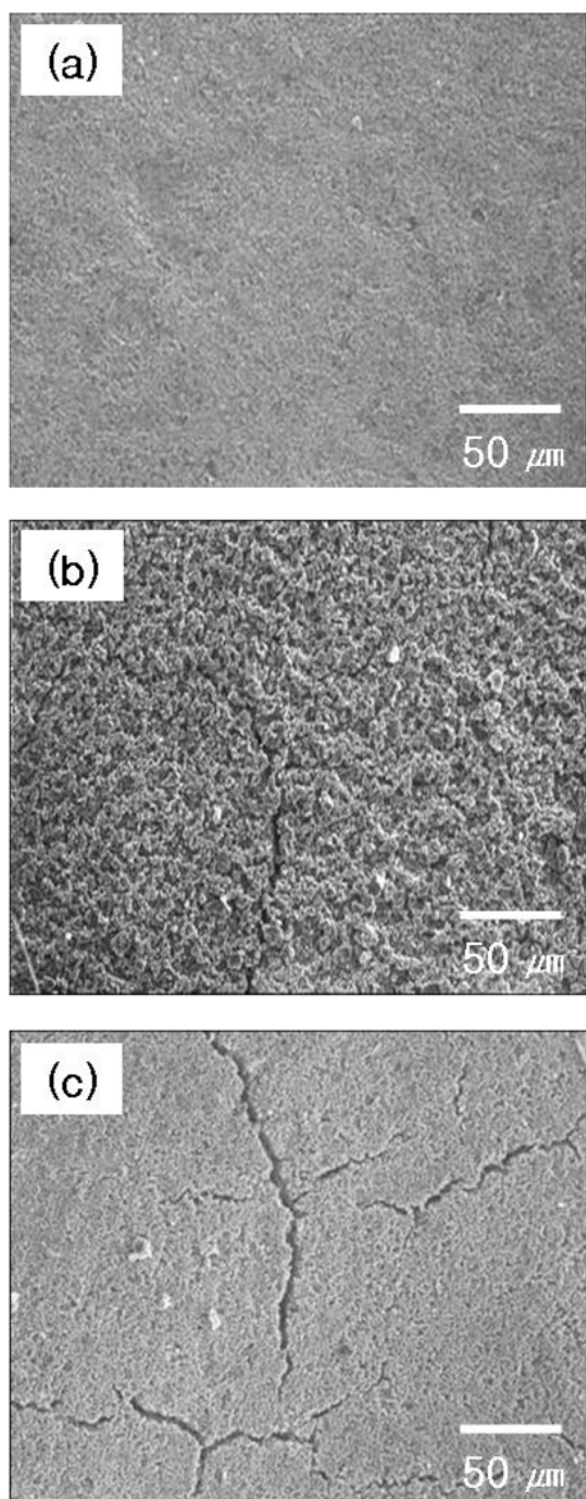


Fig. 2. Microstructure of filter surface: (a) normal; (b) after thermal shock test (500, 50 times); (c) after thermal shock test (500, 100 times).

and a rapid decrease in efficiency was found as the aging temperature was increased. The optimum temperature and temperature window did not change for the reduction of NO_x. On the other hand, when the catalyst was exposed to SO_x (Fig. 3(b)), the decrease of efficiency was initiated from 450 °C and we found out not only an abrupt decrease of efficiency but also a variation of the optimum temperature

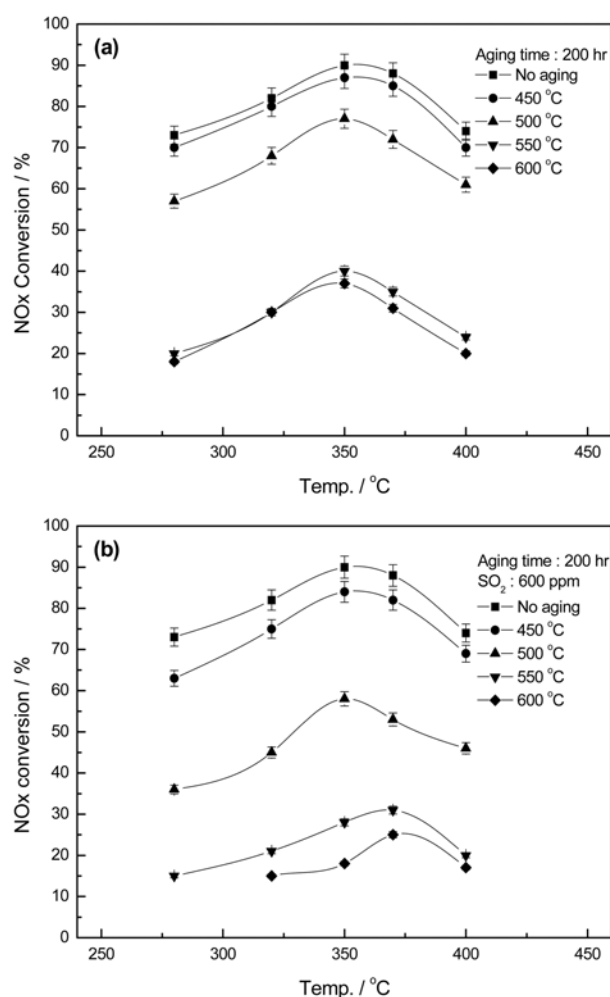


Fig. 3. Efficiency of catalysts in reduction of NO by ammonia after durability test: (a) after thermal durability test; (b) after thermal & chemical durability test.

and temperature window above 500 °C.

The crystal structure, microstructure and active sites of the catalytic filter were examined to find out the main factor of catalyst deactivation. The crystal structure and microstructure of catalytic filters, which were heated to a high temperature, did not change. However, the active sites of the catalyst were decreased as the aging temperature was increased (Fig. 4). Fig. 4 shows the variation of the IR-spectra of catalytic filters with adsorbed ammonia under ambient conditions for 1 h after durability tests. The chemisorption of ammonia with the V = O double bond is known to create Lewis acid sites and Brønsted acid sites which appear at 1,605 and 1,425 cm⁻¹, respectively [11]. These sites are the active sites of the V₂O₅ catalyst. From the results in Fig. 4, we could estimate that intensity of an active site was decreased because the bond strength of V = O double bond was weakened by temperature.

In addition, we could confirm that adsorption of sulfur on the surface of the catalyst accelerated the degradation of the catalyst from the chemical composition of the catalytic filter heated to a high temperature (Table 2).

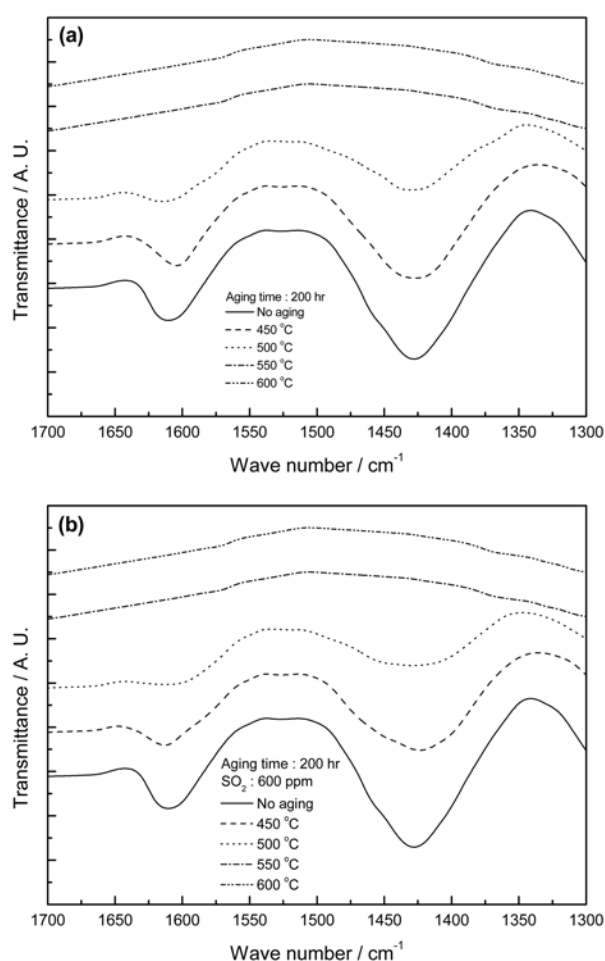


Fig. 4. FT-IR spectra of catalytic filter with adsorbed ammonia after durability tests: (a) after thermal durability test; (b) after thermal & chemical durability test.

Conclusions

Ceramic filters were fabricated using cordierite powder and they were coated with V_2O_5 catalyst by a vacuum impregnation method. The ceramic filters had an apparent porosity of 58%, a compressive strength of 10 MPa, and a pressure drop of 1,200 Pa at a face velocity of 5 cm/s and 400 °C. These values are sufficient to apply the filters to the removal of hazardous gases in an incineration system, etc. In the tests, thermal shock was the major factor which decreased the durability of filter. However, a pressure shock did not deteriorate the durability of a filter.

Table 2. Chemical composition of catalytic filter before & after heating at 600 °C (wt%)

Components	Al_2O_3	MgO	SiO_2	V_2O_5	Etc.	S
Before test	33.36	10.95	48.48	5.04	2.15	0.012
After test	33.97	10.41	47.83	5.24	2.12	0.432

Thermal shock caused the formation of cracks on the surface of filter. These will bring about an increase of the baseline differential pressure by depth filtration of dust and reduce the durability of the filter. The catalyst was degraded as the aging temperature was increased. We could confirm that the important reason for the degradation of the catalyst was a decrease of active sites by the thermal stress. Also the intensity of active site was decreased because the bond strength of the $V=O$ double bond was weakened by the high temperature. Moreover adsorption of sulfur on the surface of the catalyst accelerated the degradation of the catalyst.

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