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Development of high-performance SO_2 trap materials in the low-temperature region for diesel exhaust emission control

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ABSTRACT

Growing concern about sulfur dioxide (SO_2) poisoning NO_x removal catalysts has resulted in the development of desulfurization materials for SO_2 trap. In this study, a series of high-specific-surface-area manganese oxide (HSSA MnO_2) were selected as desulfurization materials and characterized by nitrogen adsorption and SEM. HSSA MnO_2 has good SO_2 capture performance over a wide temperature range. At low temperature, SO_2 capture capacity and adsorption rate increase with the specific surface area and HSSA MnO_2 showed high SO_2 capture performance. The effect of temperature on sulfate rate of HSSA MnO_2 can be explained by the grain model. The gradient of sulfate rate constant decreases with increasing the reaction temperature, and there is a sudden drop at 500 °C. The SO_2 capture performance of regenerated HSSA MnO_2 decreases sharply because of physical damage by calcination at high temperature.

1. Introduction

Sulfur dioxide (SO_2) from diesel exhaust is one of the main air pollutants. Besides, SO_2 from exhaust gas always poisons the sulfur-sensitive NO_x removal catalysts, especially the lean NO_x trap (LNT) in the diesel exhaust system. It is reported that the capacity of LNT is strongly reduced by SO_2, because sulfates are more stable than nitrates [1–4]. In tradition, the main way to remove SO_2 from diesel exhaust is fuel upgrades by hydrodesulfurization. However, it is still a challenge to find appropriate solutions to prevent NO_x removal catalyst from being exposed to SO_2 for the sulfur content of diesel varying from tens of ppm to hundreds of ppm.

Currently, compact SO_2 trap upstream of NO_x conversion device has been proposed to improve the longevity of NO_x removal catalysts against SO_2 poisoning in the diesel exhaust system [5–9]. The SO_2 discharge is about 160 g (10 ppm sulfur in diesel) for about 30,000 km of one year for a diesel engine, and the levels of sulphation for SO_2 trap should be at least 20% of weight increase. However, the traditional materials, such as calcined limestone [10], MgO [11] and hydrotalcite-like compounds [12,13], don't have enough SO_2 trap capacity for their application in compact SO_2 trap. Therefore, new materials with sufficient performances should be developed.

With the diesel engine technology developed, the maximum temperature of diesel exhaust is decreased and the temperature is limited from 200 °C to 500 °C. Unfortunately, limited studies have been reported in the literature on desulfurization materials with low temperature activation. Kasaoka et al. [14] focused on improving the reaction activity using complexes based on CuO at 350 °C. Tseng and Wey [15] investigated the SO_2 oxidation activity of copper oxide supported on activated carbon at the range of limited temperature between 200 °C and 450 °C. Rubio and Izquierdo [16] studied the SO_2 removal performance of coal fly ash based carbons at flue gas conditions and the amount of SO_2 removed is 13 mg/g by the Lada activated sample at 100 °C and the present of 1000 ppmv SO_2, 5% O_2, 6% H_2O gas conditions after 24 h. Nishioka and Yoshida [17] investigated the reaction activity of SO_2 trap catalyst with a noble metal under low temperature conditions and the amount of trapped sulfur is about 18 g/2 l-catalyst at 250 °C. Kylhammar et al. [18] investigated the SO_2 trapping capacity of CeO_2-based materials at 250 °C and the fresh sample can storage about 19 mg_{SO2}/g_{CeO2}. In these studies, the SO_2 trap capacities of materials are very small in low temperature range.

In the previous studies [19], it has been found that the $CaCO_3$ materials have good reactivity with SO_2 at 650 °C. However, the sulfation rate declines under low temperature conditions for the

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Nomenclature

P	SO_2 capture performance per unit mass, $g_{SO2}/g_{material}$
s	weight, mg
t	time, s
X	reaction ratio, %
M	amount of material, g/mol
C	molar concentration of SO_2, mol/cm^3
k	reaction rate constant, cm^4/(mol s)
r	radius at reaction surface, cm
R	radius of spherical grain, cm
ε	void fraction, %

reason that the sulfate reaction activity may be limited by the decarbonation. The SO_2 trapping performance of materials with different physical properties (for example particle diameter, pore diameter distribution and specific surface area) has been investigated [20–22]. From these studies, under low temperature conditions the materials with high specific surface area and simple reaction mechanism exhibit good SO_2 trapping performance. Manganese oxide with high specific surface area (HSSA MnO_2) and a simple sulfate reaction path ($MnO_2 + SO_2 \rightarrow MnSO_4$) was focused on as a candidate for the materials of desulfurization filter in low temperature region [23,24].

Furthermore, in the present work, basic SO_2 capture performance of was measured by a thermogravimetry (TG) device. Then, the influences of specific surface area on SO_2 capture performance of HSSA MnO_2 at low temperature were investigated under a wide temperature range of diesel exhaust. The sulfate rate constant was estimated at various reaction temperatures by using grain model. Finally, SO_2 capture performance of fresh and regenerable HSSA MnO_2 was investigated.

2. Experimental

2.1. Materials

The HSSA MnO_2 used for experiments was supplied by Japan Material and Chemical Co., Ltd. These materials were obtained by the acid treatment of raw material. In the experiments, HSSA MnO_2 materials with specific surface area 155 m^2/g, 200 m^2/g, 257 m^2/g and 300 m^2/g were selected. Commercial MnO_2 from Kanto Chemical Co., Inc. (specific surface area of 20 m^2/g) was used as a reference.

In this study, the specific surface area, pore volume distribution, and surface structure were analyzed to assess the physical characteristics of the target materials. The specific surface area of these samples was measured by the Brunauer–Emmett–Teller (BET) with the nitrogen adsorption uptake at the boiling point of nitrogen of 77 K using a capacitive measurement method. The pore-diameter was measured by nitrogen physisorption under normal relative pressure of 0.1–1.0 using the Barrett–Joyner–Halenda (BJH) method. Surface observation of the samples was conducted by scanning electron microscopy (SEM). The particle size distribution of the selected materials was determined by Malvern laser particle size analyzer.

Fig. 1 shows the distribution of pore diameter of HSSA MnO_2 with different specific surface area. The specific surface area of selected samples is 155 m^2/g, 200 m^2/g and 257 m^2/g, respectively. From the results of Fig. 1, the relatively large pore-diameter of all samples ranges from 40 Å to 100 Å. The micrograph of HSSA MnO_2 is displayed in Fig. 2. The formed-grain HSSA MnO_2 is seen to be made up of non-uniformly smooth spherical particles with a small size of 1 μm and the particle size of the materials ranges from 0.76 μm to 2.51 μm, as seen in Table 1.

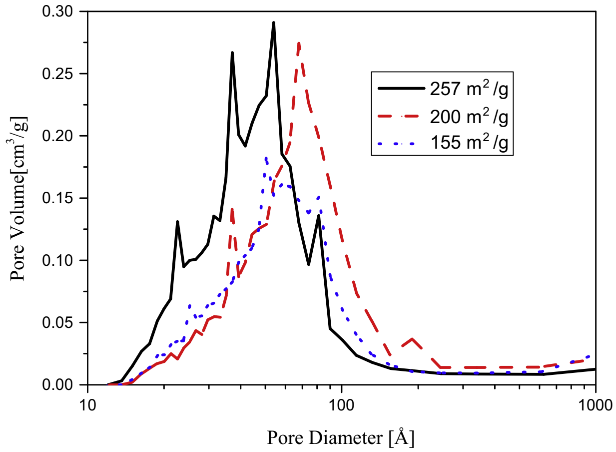

Fig. 1. Distribution of pore diameter of HSSA MnO_2 with different specific surface area: 155 m^2/g, 200 m^2/g and 257 m^2/g.

2.2. Thermogravimetric measurements

Thermogravimetry (TG) was used in this study to measure the effectiveness of the sulfate reaction of HSSA MnO_2. Fig. 3 shows a schematic drawing of the TG analysis experiment. The amount 50 mg of a sample on a quartz crucible was slowly (10 K/min) heated to the target temperature in the atmosphere of nitrogen, and maintained this condition for about 2 h. Reactant gas flow (500 ppm SO_2 in base N_2) was controlled by mass flow controller. The total flow gas rate was 2 l/min. During SO_2 adsorption, the gas stream was passed over the sample at target temperature for 2 h. The reaction temperature of the TG experiment ranged from 100 °C to 600 °C.

The SO_2 capture performance of samples was measured. The SO_2 capture performance per unit mass P and the conversion of samples $X_{(t)}$ are expressed by the following equations:

$$P = \frac{s_t - s_0}{s_0} \quad [g_{SO_2}/g_{MnO_2}] \tag{1}$$

$$X_{(t)} = \frac{M_{MnO_2}}{M_{SO_2}} \cdot \frac{s_t - s_0}{s_0} \quad [g_{SO_2}/g_{MnO_2}] \tag{2}$$

P is the SO_2 capture performance per unit mass [g_{SO2}/g_{MnO2}], s_0 is the initial weight [mg], and s_t is the weight after t seconds [mg], M_{MnO2} is the molar mass of MnO_2 [g/mol], M_{SO2} is the molar mass of SO_2 [g/mol].

3. Results and discussion

3.1. Basic sulfate performance of HSSA MnO_2 particle

Fig. 4 shows the influence of sulfate reaction temperature on SO_2 capture performance of HSSA MnO_2. The SO_2 capture