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The effect of NO pre-oxidizing in a temperature-swing-adsorption system for diesel NO_x aftertreatment—Mechanisms to enhance its performance

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ABSTRACT

Adsorption/desorption tests and infrared (IR) absorption analysis, using simulated gas mixtures, were conducted. The adsorbent used was a Mn–Cu mixed oxide. For the adsorption/desorption test, gas mixtures composed of NO, NO_2, O_2, and H_2O, balanced with N_2, were fed to the adsorbent pellets at 100 °C in the adsorption process. In the subsequent desorption process, the temperature of the adsorbent was elevated to 300 °C, N_2 was used as the carrier gas, and the desorbed gas compositions were determined. For the IR absorption analysis, the above-mentioned gas mixtures were fed to the ground Mn–Cu mixed oxide, after which the powder samples were analyzed by the attenuated total reflection method. It was found that the NO_2 adsorption presented larger capacity and an increase in the formation of a surface compound that desorbs at temperatures as low as 150 °C, than the adsorption of the NO and O_2 mixture. The IR absorption analysis suggested that these results could be attributed to the larger fraction of monodentate nitrates, as an adsorption state, in the case of the NO_2 adsorption. Water vapor contained in the gas mixture increased the NO_2 adsorption capacity by forming a surface compound similar to manganese nitrate hydrate.

1. Introduction

Diesel engines have significant benefits, such as high thermal efficiency and high durability, which have led to their use in a wide variety of applications, some of which are: engines for large trucks, tractors, ships, and power plants, and components to complement solar and wind power in a microgrid [1]. Their benefits have become even more important as the pressure to reduce CO_2 emissions and fossil fuel consumption, and to purify exhaust gases, has increased to address mounting environmental concerns. Thus far, the most promising techniques for NO_x aftertreatment have been lean NO_x traps (LNT) [2–6], and selective catalytic reduction (SCR) systems [2,6–9]. Since these systems require either additional fuel or the use of a urea solution to reduce NO_x emissions, they represent a couple of percentage points of the total operating cost of the diesel engine [6].

We have been studying a NO_x aftertreatment system combining nonthermal plasma (NTP) technology with a temperature-swing-adsorption (TSA) system driven by engine waste heat [10,11]. This system can treat NO_x emissions at a low energy cost. Fig. 1 shows the basic concept of this approach. The two adsorbers shown in Fig. 1 perform alternating processes of adsorption and desorption. Using a small volume of low-O_2 gas as a carrier for desorption, a highly concentrated NO_x can be obtained, which is further reduced by the NTP treatment. Injecting the NO_x-containing gas mixture that survives NTP, into the engine intake can further reduce the NO_x emissions because the injected NO_x reduces the Zeldovich NO formation [12].

To improve the TSA performance, we tried to enhance the NO_x adsorption by converting NO, the major constituent of NO_x in the exhaust gas, to NO_2 before it reached the adsorber (doted box in Fig. 1). This technique was shown to be very effective [11]; however, the reason for this is not clearly understood. Several studies have been conducted to understand the mechanisms of NO and NO_2 adsorption on Mn and/or Cu oxides; for example, Mn, Cu, or Ni ion-exchanged ZSM5 [13–15], MnO_2 on NaY [16], Mn and/or Cu oxides combined with/without other transition metal oxides [9,17–27], MnO_x on carbon fibers [7]. However, to find a specific answer to our question, investigations must be conducted under the operational conditions of our NO_x adsorption/desorption system: temperature ranging from 80 to 125 °C with approximately 7–10 vol% water vapor for adsorption and 100–300 °C, without any reducing agent, for desorption.

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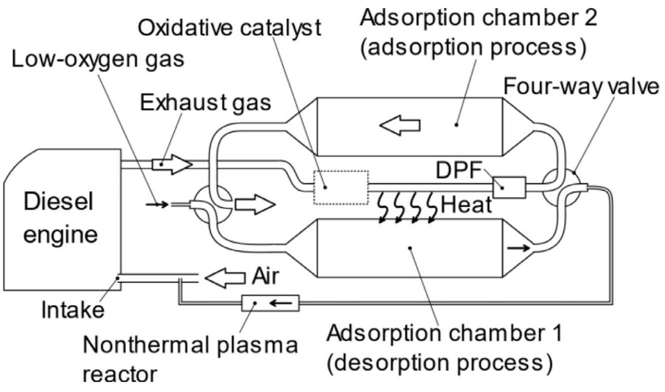

Fig. 1. Diagram of a NO_x aftertreatment system.

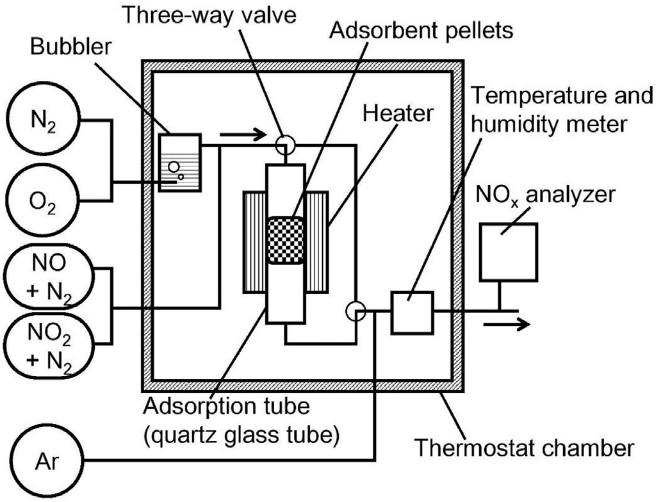

Fig. 2. Experimental apparatus for the adsorption process.

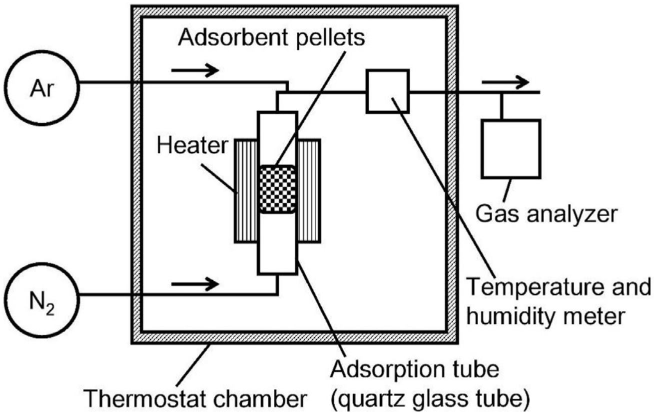

Fig. 3. Experimental apparatus for the desorption process.

2. Experimental method

2.1. Adsorption/desorption tests using simulated gases

2.1.1. Materials and apparatus

Experiments consisted of an NO and NO_2 adsorption process, followed by a desorption process using a programmed temperature profile. The adsorbent used was a mixture of copper and manganese oxides (N-140, 1.2–2.4 mm granular pellets, Clariant Catalysts (Japan) K. K.), composed of 20 wt% CuO and 50 wt% MnO_2. The rest is moisture and Cu/Mn oxides with an undetermined valence. These mixtures are commercially sold for CO oxidation and volatile organic compound removal. The above-described adsorbent was labeled N-140, and this designation is used throughout this paper. The calculated Brunauer–Emmett–Teller (BET) specific surface area was 151 m^2/g. This adsorbent was identical to the one we have previously used in our NO_x aftertreatment systems [10,11]. X-ray diffraction (XRD) spectra showed a broad peak in the range of 36°–39°, corresponding to the CuO (monoclinic) crystal. Diffraction patterns from crystals that contained Mn were not observed, which indicated that the Mn-containing compounds were nearly amorphous.

Figs. 2 and 3 show the experimental apparatuses used for the adsorption and the desorption process, respectively. In the adsorption process, adsorbent pellets were packed in a quartz adsorption tube, which inner and outer diameters were 12.5 and 16 mm, respectively. The temperature of the adsorbent pellets was maintained by controlling the surface temperature of the adsorption tube with a surrounding heater. The temperature difference between the inside and outside of the tube was negligible. Gases from cylinders of N_2, O_2, 2 vol% NO in N_2, and 2000 ppm NO_2 in N_2, were fed through mass-flow controllers to make the gas mixtures used in this experiment. When water vapor was required, a water bubbler was placed in the flow path of the O_2/N_2 mixture. Two three-way valves were assembled to serve as a by-pass for measuring the NO, NO_2, and water vapor concentrations in the gas mixtures. The apparatus, including the bubbler and other parts, was placed in a thermostatic chamber. The water vapor concentration in the gas mixtures was controlled by setting the temperature of the chamber between 45 and 60 °C. The gas mixture that exited the adsorption tube was analyzed with a temperature and humidity sensor (HygroPalm, Rotronic), and an exhaust gas analyzer (350XL, Testo AG). The gas mixtures were diluted two or three times with Ar to prevent water condensation and to reduce the concentration of NO and NO_2 so that the exhaust gas analyzer could measure them accurately.

In the desorption test, N_2 was introduced in the reverse direction of that used in the adsorption process, while the temperature of the adsorbent was controlled with a surrounding heater. The desorbed gas mixture from the adsorbent was diluted three times with Ar. Access to the tubing for adsorption and desorption was controlled by valve operation.

2.1.2. Experimental procedure

The adsorbent pellets (4.85 g: all the masses indicated in this report are those of samples fresh but before pre-conditioned) were placed in the adsorption tube. The pellets were pre-conditioned at 100 °C for 20 min and then at 300 °C for 20 min, with N_2 purging at 1 dm^3/min (at standard conditions). The adsorption process was started after the adsorbent temperature equilibrated at 100 °C, and was continued for 120 min. Immediately after the adsorption process ended, the desorption was started with the programmed temperature profile: 100 °C for 10 min, then an increase of 25 °C every 35 min, up to 300 °C. N_2 of 1 dm^3/min was used as a carrier gas.

The gas mixtures fed to the adsorbent pellets in the adsorption process consisted of 0 or 900 ppm of NO or NO_2, 0 or 10 vol% of water vapor, and 0 or 10 vol% of O_2, balanced with N_2. The total gas flow rate was 2 dm^3/min (at standard conditions). These O_2 and water vapor concentrations are typical in diesel exhaust gases. Table 1 summarizes the compositions of the simulated gas mixtures used in this work.

2.2. FT-IR analysis of the adsorbates

Adsorbent pellets (1.2 g) were ground in an agate mortar and placed in an adsorption tube. After pre-conditioning, as described

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