Synergetic effects of plasma and metal oxide catalysts on diesel soot oxidation

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ABSTRACT

The synergetic effects of a pin-to-plate corona plasma and Mn, Co and Fe oxide catalysts on soot oxidation were investigated under diesel exhaust gas conditions of 10% oxygen and 180–350 °C. The catalysts were synthesized by a precipitation method and characterized by XRD, BET surface area, SEM, EDX mapping, and temperature programmed methods of H_2-reduction, O_2-desorption and oxidation. The effects of energy injection, gas temperature, NO_x, and water vapor were investigated on the soot removal efficiency in the absence and presence of catalysts. Both tight and in-situ catalyst–soot contacts were examined. NO_x as the most hazardous pollutant in the diesel exhaust gas is completely removed in plasma. In the presence of the catalyst, the soot removal efficiency and selectivity to CO_2 enhance by up to 77 and 29%, respectively, as compared to those in the plasma alone. The highest removal efficiency and CO_2 selectivity are obtained on manganese and iron oxides at high and low temperatures, respectively. 49.3 and 17.4% enhancements of energy efficiency are observed, when 3.5% H_2O vapor or 450 ppm NO_x is added to the plasma–MnO_x catalysis system at 5.7 W and 300 °C, respectively. High energy efficiencies at very low energy injections are the advantages of this study.

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1. Introduction

Diesel engines are the most effective combustion motors used for a wide range of automotive and technical applications. However, diesel engines emit diesel exhaust particulates (DEP) basically composed of soot derived from incomplete combustion with serious problems for human health and environment [1]. Emission regulations for DEP have become increasingly stringent globally. Therefore, it is necessary to develop effective technologies for the DEP pollutant removal [2]. Diesel particulate filter (DPF) with different designs is used as the most common method to remove DEP [3]. DPFs operate in the wall flow mode including the deposition of soot onto the porous filter walls, while the exhaust flows through them. On the other hand, the loaded DPF can cause a backpressure potentially decreasing the engine efficiency. Hence, a regeneration step at above 600 °C is mandatory to thermally remove the soot deposits from the filter, while the diesel exhaust gas is typically at 180–400 °C [4,5].

An alternative technique is using catalysts in two different ways: the addition of the catalyst to the fuel in form of organic derivatives of active metals and the deposition of a catalytic coating onto the filter surface. In this way, soot particles can combust at lower temperatures [6]. Noble metals [7], transition metal oxides [8], alkaline metal oxides [9], perovskite-like oxides [10] and rare earth oxides [11] are some of the catalysts which exhibited good catalytic performances. Transition metal oxides such as MnO_x [11], FeO_x [12], CoO_x [13] and CuO_x [14] have been used as the main catalysts for soot oxidation because of their redox catalytic cycles. Most of the oxide catalysts provide enough activities for soot oxidation only at temperatures higher than 400 °C. However, in recent years, some researchers have focused on the development of catalysts to lower the catalytic oxidation temperature of the diesel soot below 300 °C [15,16].

The role of transition metal catalysts in soot oxidation reaction is oxygen transfer from their surface to the soot [17]. Therefore, a critical issue affecting the performance of catalysts for soot oxidation is the contact condition between the catalyst and soot [18,19]. Three types of soot–catalyst contacts are examined in previous studies: (I) mixing soot and catalyst with just a spatula (loose contact), (II) mixing in a mechanical mill (tight contact), and (III) passing the diesel exhaust gas containing soot over a catalyst bed (in situ con-

tact). It is reported that the results of "loose contact" and "in situ contact" are almost the same [20].

The non-thermal plasma (NTP) technology offers an innovative process for soot oxidation. In this method, the energy delivered to the system helps electrons to accelerate and gain a typical temperature of 10,000–250,000 K, while the background gas temperature does not rise significantly. The electrons collide with background molecules (N_2, O_2, and H_2O) and produce secondary electrons, photons, ions and radicals which accelerate the soot oxidation reaction [21,22]. The reaction of O atoms with carbon is estimated to be about 40 times higher than that of O_2 molecules [23]. Various types of discharges including corona [24], pulsed-corona [25] and dielectric barrier discharge [26] have been investigated. However, the process efficiency of NTP technology does not allow the achievement of both high conversion and CO_2 selectivity [27]. To overcome this limitation, an innovative technology of coupling the plasma reactor with a catalyst has been proposed.

Previous works indicate that the hybridization of NTP with a catalyst often causes a synergetic effect on the soot oxidation efficiency [28,29]. This synergetic effect can be explained by the short-living reactive species formed in the discharge [30]. It has been suggested that these species play an important role in promoting the re-oxidation of metal oxide vacancies generated in oxidation reaction in the discharge [31]. However, coupling mechanisms involved in this synergy have not been fully understood, and little information exists about the role of these reactive species [32]. Also, ozone is an important by-product in the plasma and is thermally stable up to 200 °C. Thermal and catalytic decomposition of ozone not only result in an increased energy efficiency, but also this harmful component is removed from the outlet gas stream [30].

In this work, the soot oxidation was investigated using a pin-to-plate corona plasma coupled with metal oxides in a catalytic reactor under diesel exhaust gas conditions. The effects of energy injection, temperature, and presence of NO_x and water vapor were also studied. The specific surface area, particle size, reducibility, and oxygen storage capacity of the metals (Mn, Co, and Fe) oxides are correlated with their soot oxidation activity.

2. Experimental

The catalyst samples, their characterization methods, and the plasma-(catalytic) soot oxidation variables investigated in in-situ and mostly tight contacts are summarized in Fig. 1.

2.1. Catalyst preparation

The metal oxides were synthesized by a precipitation method. Proper amounts of $Mn(NO_3)_2 \cdot 4H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ and $Fe(NO_3)_3 \cdot 9H_2O$ (all from Merck) were dissolved in 250 ml of deionized water to obtain 0.5 M aqueous solutions. 1.0 M ammonia solution was added to the solutions drop wise at room temperature under vigorous stirring to adjust the pH value at about 10. The samples were kept under moderate stirring for 6 h [33], and then centrifuged to separate their solids. The solids were washed to neutrality with deionized water, dried at 80 °C for 12 h, and calcined at 400 °C in air for 3 h.

2.2. Catalysts and soot characterization

The specific surface areas (S_{BET}) of the catalysts and soot were determined at the liquid nitrogen temperature by the adsorption and desorption isotherms of nitrogen using a Quantachrome CHEMBET-3000 apparatus. Prior to BET and H_2-temperature programmed reduction (H_2-TPR) measurements, each sample was pretreated at 300 °C for 1 h in a flow of 10 sccm of nitrogen, to

remove possible impurities, e.g. adsorbed H_2O. The average particle sizes were calculated from BET specific surface areas, assuming mono-dispersed spherical nanoparticles.

The surface morphology of the samples was determined by a scanning electron microscopy (SEM), using a Zeiss Sigma instrument. The catalysts uniform dispersion in the soot was measured by energy dispersive X-ray (EDX) elemental mapping.

X-ray diffraction (XRD) patterns of the catalysts were obtained by a Philips PW 1800 diffractometer using Cu-Kα radiation (40 kV/30 mA). The diffractograms were recorded from 2θ of 10–100° with a step-size $\Delta(2\theta)$ of 0.02° and a time of 0.35 s per step. The oxide phase analyses were done based on JCPDS files. The mean crystallite size of the catalysts was calculated using the Scherrer's equation (Eq. (1)).

$$d_{XRD} = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where, k is a constant equal to 0.89, λ is the wavelength of the used X-ray equal to 0.15418 nm, β is the half-peak width and θ is the diffraction angle of main peak.

The H_2-TPR experiments of the samples were conducted in the CHEMBET-3000 apparatus. 10 sccm of 7% H_2 in Ar was passed through 25 mg of each sample, while the temperature was linearly increased at a rate of 10 °C/min to 1000 °C. The thermal conductivity detector (TCD) of the apparatus monitored the H_2 consumption in the TPR reactor. The TCD signal was calibrated by reduction of Ag_2O under the same conditions as the TPR test.

The O_2-temperature programmed desorption (O_2-TPD) of the catalysts was performed using the same apparatus as BET surface area measurement. Prior to each TPD run, 25 mg of each sample was pretreated at 300 °C for 1 h, and then cooled down to room temperature, in a flow of 10 sccm oxygen. This let the catalysts to be fully oxidized and adsorb oxygen on its surface. The catalyst was then exposed to a flow of 10 sccm He for 30 min at room temperature, to purge the reactor and clean the surface of catalyst from the weakly bonded oxygen. Finally, the sample was heated to 1000 °C at a rate of 10 °C/min under the same flow of helium and the desorbed oxygen was detected by the TCD.

The temperature programmed oxidation (TPO) of 7 mg catalyst in tight contact with 3.5 mg soot was also performed. The feed gas with a flow rate of 300 sccm consisting 10% O_2 in N_2 was controlled by two mass flow controllers. In all TPO runs, the temperature was increased to 600 °C at a rate of 10 °C/min. The effluent gases of each TPO run were analyzed by a Fourier-transform infrared spectrometer (FTIR, Bruker Vector 22).

2.3. Plasma-catalytic oxidation of soot

Fig. 2A shows the plasma-catalytic soot oxidation system including a pin-to-plate corona plasma reactor, a home-made DC power supply (0–20 kV), a gas supply manifold, and the analytical instrumentations. 300 sccm of the feed gas containing 10% O_2 in N_2, similar to the oxygen concentration in the diesel exhaust gas, was passed through the reactor. The air and N_2 gas flow rates, to obtain such a feed gas, were regulated by Unit mass flow controllers. To investigate the effects of 3.5% H_2O vapor on the soot oxidation performance, air was passed through a bubbler containing deionized water at room temperature. The reactor effluent gas was analyzed by the on-line FTIR equipped with a gas cell. The FTIR spectra were obtained with 4 cm^{-1} resolution every 30 s. A Carle 400-A gas chromatograph (GC) equipped with a methanizer comprising a Ru/Al_2O_3 catalyst at 420 °C was used for quantitative analysis of the reactor effluent gases. The inlet gas was also analyzed by bypassing the reactor feed directly into the FTIR and GC, using two 3-way valves. Based on the reactor volume and feed flow rate, the residence time in the plasma-catalytic reactor is 0.94 s.