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Combined promoting effects of platinum and MnO_x–CeO_2 supported on alumina on NO_x-assisted soot oxidation: Thermal stability and sulfur resistance

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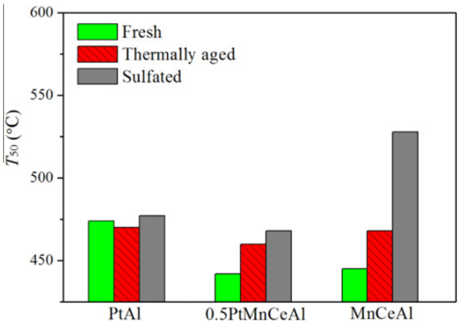
HIGHLIGHTS

- ▶ Modification of MnO_x–CeO_2 enhances the soot oxidation activity of Pt/Al_2O_3 in NO + O_2.
- ▶ The loading amount of Pt on Pt/Al_2O_3 catalyst can be halved by addition of MnO_x–CeO_2.
- ▶ The modified catalyst shows high activity after calcination at 800 °C for 100 h.
- ▶ It also exhibits superior sulfur resistance after treating in SO_2 at 350 °C for 50 h.
- ▶ The activity of the sulfated catalyst is facilitated by the Pt-sulfates interaction.

GRAPHICAL ABSTRACT

Light-off temperatures of different catalysts during the soot-TPO in NO + O_2.



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ABSTRACT

MnO_x–CeO_2 mixed oxides were introduced into Pt/Al_2O_3 catalyst to reduce the amount of platinum and improve the catalytic activity for soot oxidation in presence of NO_x. The catalysts were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM), CO chemisorption, thermogravimetric (TG) analysis, Fourier transform infrared spectroscopy (FTIR), H_2 temperature-programmed reduction (H_2-TPR), NO temperature-programmed oxidation (NO-TPO) and soot temperature-programmed oxidation (soot-TPO). Due to the superior redox property, the introduction of MnO_x–CeO_2 mixed oxides effectively enhanced the catalytic activities of Pt/Al_2O_3 catalyst for NO oxidation and hereby for soot oxidation in NO + O_2. The Pt/MnO_x–CeO_2/Al_2O_3 catalyst also exhibited high activities after the thermal ageing and sulfur poisoning, which are related to the intrinsic characteristics of MnO_x–CeO_2/Al_2O_3 and Pt as well as their synergistic effects. The deactivation mechanisms of different catalysts (Pt/Al_2O_3, MnO_x–CeO_2/Al_2O_3 and Pt/MnO_x–CeO_2/Al_2O_3) were discussed.

1. Introduction

The deleterious effect on human health of particulate present in diesel emissions has resulted in the formulation of restrictive legislation both in the EU and the US. Such particulate matter comprises of carbonaceous soot particles and other smaller molecular compounds, many of which are toxic. Due to the environmental and health impacts of diesel soot and the pressure to comply with the emissions regulations, efforts to reduce the diesel soot emissions are ongoing and remaining as a challenging topic [1]. Trapping on filter followed by oxidation is an efficient means of elimination of soot particulate matters. However, oxidation of typical diesel engine exhaust gas to CO_2 in the uncatalyzed soot filter generally occurs at around 600 °C, which is obvious higher than the exhaust temperature of diesel vehicles [2]. The use of a catalytic trap performing both filtration and catalytic combustion of soot appears to be an effective solution. Among the catalysts investi-

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gated, Pt exhibits a high level of catalytic activity by oxidizing NO in the exhaust gas to NO_2, which has remarkable effects on the oxidation of soot [3–5].

Though platinum catalysts exhibit good activity for soot oxidation, the high cost of platinum has made it necessary to find out appropriate alternatives. According the oxide catalysts reported, MnO_x–CeO_2 mixed oxides with much lower price have evidenced high soot oxidation activities in both excess O_2 [6,7] and NO + O_2 [8,9]. The incorporation of manganese cations into the ceria lattice greatly improves the oxygen mobility in the mixed oxides. Additionally, this catalyst is not only advantageous in the catalytic oxidation of NO, but is also associated with the high NO_x storage capacity at low temperatures, which can release abundant NO_2 at appropriate higher temperatures. To try to solve the disadvantage of feasibly sintering of the mixed oxides at high temperatures, Al_2O_3 has been introduced to significantly increase the textural stability of MnO_x–CeO_2 with relatively high dispersions of MnO_x and CeO_2 after thermal ageing [10,11].

Thermal ageing and sulfur poisoning are two critical deactivation factors for soot oxidation catalysts. Sintering and coalescence of active sites at high temperatures and the blocking effect of sulfates may lead to severe deactivation of platinum catalysts [12]. It has been reported that the introduction of CeO_2 would lead to a stabilization of the Al_2O_3 support and the platinum particles towards sintering [13,14]. However, ceria is well known to react with SO_2 over a wide range of temperatures. When exposed to even small amounts of sulfur containing compounds, the performance of cerium oxide will be substantially diminished [15]. Meanwhile, Pt catalysts for NO oxidation have been reported to have some resistibility to sulfur poisoning [16]. Thus, the partially replacement rather than completely substitution of Pt by MnO_x–CeO_2 may be a plausible way for preparing promising soot oxidation catalysts.

In the present study, MnO_x–CeO_2 mixed oxides were introduced to Pt/Al_2O_3 catalyst with a halved loading amount of platinum. Thermal ageing and sulfur poisoning treatments were performed to examine the stability of the catalysts. In order to explore possible modification mechanism of the mixed oxides and different deactivation mechanisms, the catalysts were characterized by a series of structural and surface property measurements.

2. Experimental

2.1. Catalyst preparation

MnO_x–CeO_2–Al_2O_3 mixed oxides (MnCeAl) with a Mn/Ce molar ratio of 15:85 and a weight ratio of (Mn_2O_3 + CeO_2):Al_2O_3 = 1:2 were synthesized by a citric acid-aided sol–gel method as described in [9] using $Ce(NO_3)_3 \cdot 6H_2O$ (Yili, Beijing) and $C_4H_6MnO_4 \cdot 4H_2O$ (Chemical Reagents, Beijing) as the precursors. Cerium nitrate and manganese acetate were dissolved in deionized water and mixed with γ-Al_2O_3 powders (BASF, 150 m^2/g). Citric acid was added as the complexing agent with twice as the metal ions including Ce^{3+} and Mn^{2+}. Polyglycol was then added at 10% of the weight of citric acid. The solution was sufficiently stirred and heated at 80 °C until a porous gel was formed. The gel was dried at 110 °C overnight followed by decomposition at 300 °C for 1 h and calcination at 500 °C for 5 h under static air in a muffle. As a reference, the pure alumina also experienced the same calcination process.

The supported platinum catalysts were prepared by successively impregnating the obtained supports (MnCeAl and Al_2O_3) with $Pt(NO_3)_2$ solution (27.82 wt.%, Heraeus) as the precursor. The nominal loading amount of Pt was 1 wt.% on Al_2O_3 and 0.5 wt.% on MnCeAl. The received catalysts were denoted as PtAl–F and 0.5PtMnCeAl–F, respectively.

The as-received catalysts were treated at 800 °C for 100 h in static air to obtain the aged catalysts with a suffix of "–A", and the sulfated samples with a suffix of "–S" were obtained by treated the as-received catalysts at 350 °C in 100 ppm SO_2/air for 50 h.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were determined by a Japan Science D/max-RB diffractometer employing Cu–Ka radiation (λ = 0.15418 nm). The X-ray tube was operated at 40 kV and 30 mA. The X-ray diffractograms were recorded at 0.02° intervals in the range of $20° \leqslant 2\theta \leqslant 80°$ with a scanning velocity of 4°/min.

The specific surface areas of the samples were measured using the N_2 adsorption isotherm at −196 °C by the four-point Brunauer–Emmett–Teller (BET) method using an automatic surface analyzer (F–Sorb 3400, Gold APP Instrument). The samples were degassed at 200 °C for 2 h prior to the measurements.

Platinum dispersion of the catalysts was carried out on the Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD). For each experiment, approximately 50 mg of catalyst was placed in an U-shaped quartz tube (i.d. = 10 mm) and reduced in a flow of 10% H_2/Ar (50 ml/min) while ramping the temperature up to 400 °C at the rate of 10 °C/min, and then held at 400 °C for 30 min in flowing He (50 ml/min) for proper degassing. After that the sample was cooled down to 25 °C, the loop gas of 10% CO/He (20 ml/min) was pulsed over the sample and the TCD signal was recorded until the peak area became constant. In the calculation of the dispersion, adsorption of 1 CO molecule per accessible Pt atom was assumed. The percent dispersion was calculated by dividing the number of exposed surface Pt atoms (as determined by CO chemisorption) by the total amount of Pt in the catalyst. Mean Pt particle size (D_{Pt}) was determined from CO chemisorption data by assuming all surface Pt particles were spherical in shape.

H_2 temperature-programmed reduction (H_2-TPR) was performed on the Micromeritics AutoChem II 2920. Prior to the experiment, 50 mg of sample was treated in flowing He (50 ml/min) at 400 °C for 30 min for proper degassing, and then cooled down to RT and flushed for 10 min. Finally, the atmosphere was changed to 10% H_2/Ar (50 ml/min) and the reactor temperature was raised up to 800 °C at a heating rate of 10 °C/min. H_2 consumption during the experiment was monitored as TCD signals by chemisorb.

Transmission electron microscope (TEM) images were taken using a FEI Tecnai G^2 20 with an acceleration voltage of 200 kV. Mean Pt particle size was calculated from TEM images by averaging 50 points of Pt particles.

Infrared (IR) spectra of CO adsorbed on the samples were recorded on a Nicolet 6700 FTIR spectrometer equipped with a MCT detector. After pretreatment in N_2 (50 ml/min) at 500 °C for 0.5 h, the sample was then cooled down to RT. The spectra were taken after exposing the catalyst to 1% CO/N_2 (50 ml/min) for 30 min followed by purging with N_2.

Thermogravimetric (TG) analysis experiments were conducted on a METTLER Toledo thermogravimetric analyzer. For each experiment, 15 mg of the sample was heated from ambient to 1000 °C at a heating rate of 10 °C/min. Reaction was carried out in N_2 (50 ml/min) at the gauge pressure of 0.1 atm (10.1 kPa). The chamber blowing gas, N_2 (99.99% purity), was fixed at a flow rate of 20 ml/min.

The NO temperature-programmed oxidation (TPO) tests were carried out in a fixed-bed reactor with the effluent gases monitored by an infrared spectrometer (Thermo Nicolet IS10). 100 mg of sample was diluted with 300 mg of silica pellets, and then were sandwiched by quartz wool in a tubular quartz reactor. A gas mixture of 1000 ppm NO/10% O_2/N_2 (500 ml/min) was fed and the reactor temperature was ramped to 600 °C at a heating rate of 10 °C/min.