Sulfation of Pt/Al$_2$O$_3$ catalyst for soot oxidation: High utilization of NO$_2$ and oxidation of surface oxygenated complexes

Shuang Liu [a], Xiaodong Wu [a,*], Duan Weng [a], Min Li [a], Jun Fan [b]

[a] The Key Laboratory of Advanced Materials of Ministry of Education, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China
[b] The Administrative Centre for China's Agenda 21, Beijing 100038, China

ABSTRACT

The sulfated Pt/Al$_2$O$_3$ catalyst was synthesized by impregnating H$_2$SO$_4$ on the Pt/Al$_2$O$_3$ catalyst. It exhibits higher catalytic activity than Pt/Al$_2$O$_3$ for soot oxidation under loose contact conditions in a feed flow containing NO and O$_2$. Further studies ascribe its good activity to a synergistic effect between sulfate species and platinum. Firstly, the electronegative sulfate species may improve the oxidation-resistance of metallic platinum in the oxidizing atmosphere, which is important for achieving high NO $\leftrightarrow$ NO$_2$ $\leftrightarrow$ soot recycling efficiency; Secondly, the sulfate species inhibit the NO$_x$ adsorption on the alumina support, leading to a preferential adsorption of NO$_x$ on the surface of soot rather than on the catalyst, and thus provide more chances for NO$_2$-soot reaction to generate the surface oxygenated complexes (SOCs); Finally, the sulfate species can promote the further decomposition of these SOCs species, resulting in a high catalytic efficiency for soot oxidation.

© 2013 Elsevier B.V. All rights reserved.

1. Introduction

The different legislations dedicated to diesel particulate matter (PM) emissions of vehicles (for Europe, 0.005 g of particulates/km for passenger cars since 2009) have led to the development of different after-treatment technologies. PM is mainly constituted by carbonaceous particles (often called soot), originated from the incomplete in-cylinder oxidation of the fuel, with diameters ranging from few nanometers (10–20 nm) to up to hundreds of nanometers [1,2]. Diesel particulate filters (DPFs) are the most common devices for the collection of particulate matter for on-board diesel exhaust after-treatment. However, they eventually become blocked as the soot accumulates on the filter. The most plausible method for regenerating the filter is to use a catalyst that promotes soot oxidation at exhaust gas temperatures under engine operating conditions [3,4]. Under practical conditions occurring in a catalytic DPF, good contact conditions are very difficult to be reached due to the different orders of magnitude of the soot particle and the catalyst cluster sizes, which clearly hinder the overall activity of the catalyst. It has been observed that for the catalysts without high mobility, a loose-contact mode obtained by mixing soot and catalyst with spatula is comparable with the practical contact mode [5]. In this condition, the most of the carbon atoms are in contact with gaseous phase and, consequently, the soot oxidation temperature can be significant reduced due to the NO$_2$ produced over the catalyst [6,7]. Among the catalysts investigated, Pt exhibits a high level of catalytic activity by oxidizing NO in the exhaust gas to NO$_2$ [3,4], and Pt catalysts typically consist of Pt nanoparticles dispersed on a porous alumina support.

The presence of sulfur-containing compounds in fuel and lubricants has been reported to favor the formation of thermally stable sulfate species on the catalyst supports, and sulfur may also affect the metal functionality for NO and soot oxidation [3,8]. It has been reported that Pt catalysts supported on non-basic metal oxides (Ta$_2$O$_5$, Nb$_2$O$_5$, WO$_3$, SnO$_2$ and SiO$_2$) show high activities toward the oxidation of soot in the presence of SO$_2$, which is attributed to their non-basicity and negligible affinity toward SO$_3$ (or H$_2$SO$_4$), resulting in less poisoning of the supported Pt [3,5]. Then the influence of sulfur will be especially significant for the catalysts with supports that have high affinity for sulfur, such as Al$_2$O$_3$ [8].

Since NO$_2$ is determinant for initiating and continuing soot oxidation in the loose-contact mode, many efforts were focused on obtaining active catalysts for NO$_2$ production [9,10]. It has only been recently reported that the catalytic activity for NO oxidation did not exactly match the soot oxidation capacity of some CeO$_2$-based catalysts [11,12]. In our recent study, it was also observed that on the sulfated Pt/Al$_2$O$_3$ catalyst, the NO$_2$-assisted mechanism was no longer the sole variable for the catalytic oxidation of soot. It is suggested that a synergistic effect between platinum and sulfates on the sulfated Pt/Al$_2$O$_3$ catalyst may accelerate some rate-limiting steps, and the specific mechanism remains to be investigated [13].

---

* Corresponding author. Tel.: +86 10 62792375; fax: +86 10 62792375.
E-mail address: wuxiaodong@tsinghua.edu.cn (X. Wu).

Therefore, a systematic study is required about what kind of factors, whether it is surface/textural properties or different reaction pathways on the sulfated Pt/Al_2O_3 catalyst that influence the catalytic oxidation of soot in the presence of NO_x. For this purpose, three different samples were prepared as Pt/Al_2O_3, sulfated Pt/Al_2O_3 and sulfated Al_2O_3. The catalysts were characterized by a series of structural and surface property measurements, and further insight into the catalyzed soot oxidation mechanism was gained based on some in situ experimental results.

2. Experimental

2.1. Materials

The Pt/Al_2O_3 (PtAl) catalyst was prepared by impregnating $Pt(NO_3)_2$ (27.82 wt.%, Heraeus) on γ-Al_2O_3 powders (BASF, 150 m^2/g). The nominal loading amount of Pt was 1 wt.%. The impregnated powders were submitted to drying at 110 °C overnight and calcination at 500 °C for 2 h. The H_2SO_4-modified catalyst (SPtAl) was prepared by impregnating H_2SO_4 (98%, Beijing Modern Eastern) on the Pt supported alumina catalyst with a nominal weight ratio of H_2SO_4:Al_2O_3 = 1:19. Both catalysts were calcined at 500 °C for 2 h. As a reference, a 5 wt.% H_2SO_4-modified alumina (SAl) was prepared.

Printex-U (Degussa) was used as a model soot. Its particle size was 25 nm and the specific surface area was 100 m^2/g. For further comparison, soot containing various surface oxygen complexes (Nsoot) was obtained by treating the Printex-U in a 500 ppm NO_2/10% O_2/N_2 flow (200 ml/min) at 350 °C for 4 h.

2.2. Catalyst characterization

The powder X-ray diffraction (XRD) patterns were determined by a Japan Science D/max-RB diffractometer employing Cu-Kα 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 $20° \leq 2\theta \leq 80°$ 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.

CO titration experiments were conducted in a fixed bed quartz reactor via a method as described in ref. [8]. The catalysts were subjected to an oxygen exposure at room temperature with 30% O_2/N_2 (300 ml/min) for 1 h. The flow was then switched to N_2 (300 ml/min) in order to purge out any residual gases from the oxygen pre-treatment, and the reactor temperature was set to 150 °C. At this titration temperature, the flow was changed to 1% CO/N_2 (100 ml/min), and the outlet CO_2 concentration was analyzed by an infrared spectrometer (MKS 2300). The CO_2 trace was followed until it decreased to below the detection limit. The resulting CO_2 trace was integrated and, assuming a reaction stoichiometry $CO + O\text{-}Pt_S \rightarrow CO_2 + Pt_S$, the total amount of oxygen on the Pt was calculated. At 150 °C, CO can titrate the oxygen monolayer completely from Pt, and hence, the CO_2 amount formed (or the atomic oxygen removed) will be the same as the number of exposed surface Pt atoms. It is thus possible to calculate the number of surface Pt atoms from the CO titration at 150 °C and consequently the Pt dispersion (ratio of surface Pt to total Pt). Mean Pt particle size (D_{Pt}) was determined from Pt dispersion data by assuming all surface Pt particles were spherical in shape.

Transmission electron microscope (TEM) images were taken using a FEI Tecnai G^2 20 with an acceleration voltage of 200 kV. The size distribution of the platinum crystallites was determined by measuring 200 particles for each sample, and the mean Pt particle size was also calculated from these data.

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 30 min, 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.

The diffuse reflectance infrared Fourier transformed spectra (DRIFTS) were recorded on the same apparatus. All the samples were diluted with inert CaF_2 to obtain a feasible signal-to-noise ratio, and were prepared with a weight ratio of soot:catalyst:CaF_2 = 1:10:100 (Even if the sample contains only soot or catalyst, it would still be diluted with CaF_2 at the same weight ratio). After pretreatment in N_2 (50 ml/min) at 500 °C for 30 min, the sample was then cooled down to RT. Then the spectra were recorded from 100 °C to 550 °C at an interval of 50 °C in different atmospheres. The heating rate was 10 °C/min.

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.

The NO_x temperature-programmed desorption (TPD) tests were performed in the same apparatus to that used in NO-TPO tests. Prior to the test, the sample powders were exposed in 500 ppm NO_2/10% O_2/N_2 (500 ml/min) at 350 °C for 30 min then cooled down to RT in the same atmosphere and flushed by N_2. Afterwards, the NO and NO_2 desorption profiles were obtained by ramping the reactor from RT to 600 °C at a heating rate of 10 °C/min in a 10% O_2/N_2 stream.

2.3. Activity measurement

In the activity measurement, 10 mg of soot and 100 mg of sample were mixed by a spatula for 2 min for "loose contact" conditions. In order to prevent reaction runaway, 110 mg of the soot–catalyst mixture was diluted with 300 mg of silica pellets. The inlet gas mixture was either 1000 ppm NO/10% O_2/N_2 or 10% O_2/N_2 with a total flow rate of 500 ml/min, and the gas hourly space velocity (GHSV) was 30,000 h^{-1}. The activities of the catalysts for soot oxidation were evaluated in the same apparatus to that used in NO-TPO tests, and also in a temperature programmed oxidation (TPO) reaction apparatus at a heating rate of 10 °C/min. T_{50} represented the temperature at which 50% of soot was oxidized. The downstream CO_2/(CO_2 + CO) ratio during soot oxidation was defined as the selectivity to CO_2. The as-received catalysts were treated with soot under the same atmosphere from RT to 600 °C to obtain the spent catalysts with a suffix of "-s".

3. Results

3.1. Solid properties

Fig. 1 shows the XRD patterns of the catalysts. Only typical peaks of γ-Al_2O_3 are observed in the diffraction patterns of the catalysts