Full Length Article

Effect of valence state and particle size on NO oxidation in fresh and aged Pt-based diesel oxidation catalysts

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ABSTRACT

To stabilize Pt, Magnesium-modified SiO_2-Al_2O_3 materials was used to impregnate with Pt, which could strengthen the bonding effect between Pt and Mg. Before and after aging, both showed a higher dispersion. High valence state of Pt in fresh modified catalyst was unfavorable of NO oxidation, indicating that the valence state of Pt was the leader factor in fresh catalytic performance. While for the aged Mg-modified sample, its reaction temperature of 30% NO conversion lowered by around 30 °C. The Pt stabilization via interacting with Mg derives a relation that the variation of Pt valence state and its exposed sites played a significant role in fresh and aged catalytic NO activity, respectively.

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1. Introduction

It is a widespread realization that Platinum-supported diesel oxidation catalysts (DOC) are very efficient in eliminating diesel emission (unburned hydrocarbons, carbon monoxide, nitrogen oxides, particulate matter) [1,2]. Increasingly stringent environmental regulations request the lower harmful emissions, especially for NO_x (Euro VI emission limit, 0.4 g/kWh). In the case of a common diesel after-treatment system [3–6], the conversion of nitric oxide were the crucial reaction for the soot oxidation in diesel particular filter (DPF) and the low-temperature activity in selective catalytic reduction (SCR). Further, the influence of thermal aging resulting from active regeneration of DPF on the DOC performance is a topical research.

Platinum shows an excellent NO oxidation activity [7]. Here valence state and average crystallite size of Pt are the important factors in catalytic performance [8]. Our previous work [9] have investigated the effect of acid promoter (WO_3) on platinum in improving NO conversion, finding more metallic Pt on the catalyst doping tungsten. However, it have to realize that strengthening the interaction between platinum and support is a great way to develop the highly durable catalysts by bonding effect. Metal bonding is one of ways in inhibiting noble metal aggregation. BASF Corporation [10] introduced Pd and Au into the Pt-based catalyst, which showed a significantly higher CO and HC conversion obtained from New European Driving Cycle. A common idea that the addition of Pd could reduce the sintering rate of Pt particle, leads many researches performed on the Pt-Pd system [11–15]. Recently, "regenerative trapping" in the Pt-Pd bimetallic particles was termed by Carrillo [16]. PdO trapped the mobile PtO_2 and their reaction caused the formation of Pt-Pd alloy, thus leading to a trapping cycle. Other method is the covalent bonding. Interestingly, the Pt-oxide-support interaction could be strengthened with an increasing of oxygen electron density in support [17]. So the basic property of oxides were investigated due to its low O 1s core electron level. Tanabe et al. [18] investigated the sintering effect of Pt on Pt/MgO catalyst. This result of Pt L_3-edge extended X-ray absorption fine structure revealed the formation of an Mg_2PtO_4-like compound, which could anchor Pt and inhibit its aggregation. $MgAl_2O_4$ spinel supported Pt catalysts also showed a remarkable thermal stability, especially the small {1 1 1} spinel surfaces could facilitate the smaller Pt particles [19]. However, the relationship of valence state and particle size on Pt-based catalyst before and after aging remains have a room for further investigation in NO oxidation.

In this paper, the addition of Mg in support was prepared and its use to support Pt. A systematic investigation about the valence state and the particle size of Pt to reveal the origin of NO oxidation in the fresh and aged catalysts.

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2. Experiment

2.1. Catalyst preparation

$Mg(NO_3)_2 \cdot 6H_2O$ was loaded on the SiO_2-Al_2O_3 support (around 150 m^2/g) at a monolayer dispersion capacity of 10 wt% by the impregnation method. The modified support was dried at 60 °C and subsequently calcined at 550 °C for 3 h under airflow. And 1 wt% Pt was loaded on the treated powder by the same impregnation method. Following, same calcined procedures were performed. Then it wash-coated onto cylindrical cordierite monoliths (2.5 cm^3, 400 cells per square inch, Corning Ltd., USA). The total wash coat loading amount of each sample was about 160 g/L. The obtained monolithic catalysts calcined at 550 °C for 3 h in air. Finally, the treated catalysts Pt/MgO-SiO_2-Al_2O_3 were labeled as Pt/MgSA-f. The free-Mg sample was obtained by the same method and labeled as Pt/SA-f.

According to Ref. [20], the aged treatment was actually carried out to the samples in the following feed gas mixture: 600 ppm C_3H_6, 1500 ppm CO, 200 ppm NO, 5% O_2, 4% CO_2, and N_2 balance at 800 mL min^{-1} flow rate, at 670 °C for 15 h and then 250 °C for 15 h. The aged samples were named as Pt/SA-a, Pt/MgSA-a.

2.2. Catalytic evaluation

The catalytic activity measurements were carried out in a fixed bed quartz flow reactor. The reaction gases were a mixture of 200 ppm NO, 330 ppm C_3H_6, 1000 ppm CO, 10% O_2, 8% CO_2, N_2 balance, GHSV 60 kh^{-1}. Before testing, the monolithic catalyst was pretreated under the similar reaction condition at 550 °C for 3 h. The outlet NO and NO_2 were detected by Nicolet Antaris IGS-6700 gas analyzer (Thermo Fisher Scientific, USA). Reactant conversion was defined by the following Eq. (1):

$$NO\ conversion = \frac{[NO_2]_{outlet}}{[NO_x]_{outlet}} \times 100\% \tag{1}$$

where $[NO_2]_{outlet}$ and $[NO_x]_{outlet}$ stood for the outlet concentration.

2.3. Catalyst characterizations

X-ray diffraction (XRD) patterns of powdered samples were recorded with the Rigaku Ultima IV diffractometer, which employed Cu Kα radiation (λ = 1.5406 Å) in the 20° < 2θ < 80° and was operated at 40 kV and 40 mA.

The particle size of the catalysts was performed by transmission electron microscopy (TEM) measurement (Tecnai G2 F20 S-TWIN, FEI Company, US) with an acceleration voltage of 200 kV. The averaged particle size were obtained by the particle size distributions [21].

CO chemisorption was obtained to determine the dispersion of Pt. The catalyst was pretreated under H_2 flow (99.999%, 20 mL/min) at 450 °C for 30 min. After cooling to room temperature (RT), CO was pulsed up to adsorption saturation. The Pt dispersion of catalysts were determined by pulsing CO [22].

H_2-temperature programmed reduction (H_2-TPR) experiments were performed in a tubular quartz micro-reactor. 0.1 g sample was pretreated in N_2 (20 mL/min) from room temperature to 450 °C for 30 min. Then, the reduction reaction was performed from room temperature to 450 °C at a constant heating rate of 12 °C/min in a total flow of H_2 (5.0 vol.%)/N_2 mixture (20 mL/min). The reduction of CuO was used to calibrate the H_2 consumption.

X-ray photoelectron spectra (XPS) experiments were performed on an electron spectrometer (XSAM-800, KRATOS Co.) equipped with an Al Kα radiation as a primary excitation. Binding energies

shifts of the samples were calibrated using the C 1s (284.6 eV) as an internal reference.

CO-FTIR spectra were recorded on a Fourier transform infrared spectrometer (FTIR, Thermo Nicolet 6700). It was equipped with a high temperature environmental cell, which was fitted with KBr window and a MCT detector. The samples in the IR cell were pretreated at 450 °C for 30 min under 5 vol% H_2/N_2 before each experiment, and then cooling under N_2 gas. The sample was exposed to 1vol% CO/N_2 until no change of the spectrum, and the CO adsorption spectrum was collected after purging in N_2. The backgrounds were exactly subtracted from the sample and spectrums were obtained at the room temperature after CO adsorption. All the spectra accumulated 64 scans at a resolution of 4 cm^{-1}. Similarly, NO + O_2 co-adsorption FTIR was performed on this apparatus. 0.1 mg sample was diluted in 2 mg KBr. After the similar pretreatment under N_2 at 450 °C, 1000 ppm NO and 10% O_2 were introduced at 50 °C up to adsorption saturation, then the spectra in different temperature was recorded, such as 150 °C, 250 °C and 350 °C. The spectra was obtained at the steady-state condition.

3. Results and discussions

3.1. Characterization

3.1.1. H_2-TPR

Figs. 1 and 2 show the reduction of PtO_x on catalyst below 500 °C, no involving the reduction of support. A big and wide reduction peak of catalysts were divided into three peaks by the peak-fit treatment. The Peak I (115–130 °C) was assigned to the one step reduction of surface Pt^{4+} to metallic platinum. [23] Both fresh catalysts seems to be no difference in H_2 reduction amount. Peak II (165–180 °C) might result from the reduction of support through the interaction with platinum. Mg-modified support could strengthen the strong metal-support interactions (SMSI) [24], leading to its H_2 consumption increased by 13.5 μmol/g. Additionally, a reduction peak on the Pt/MgSA-f catalyst at a higher temperature, Peak III (255–265 °C), had a higher H_2 consumption of 29.8 μmol/g. It was far away the H_2 consumption of the blank sample (9.2 μmol/g). There would be thought that peak III was the reduction of bulk PtO_x, therefore the introduction of Mg on support could increase its reduction amount though the strong interaction of Mg and bulk
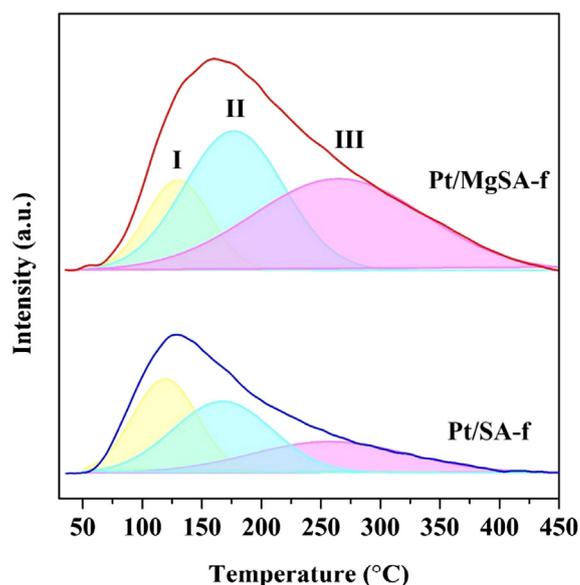

Fig. 1. H_2-TPR patterns of fresh catalysts.