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Article

Propene and CO oxidation on Pt/Ce-Zr-SO_4^{2-} diesel oxidation catalysts: Effect of sulfate on activity and stability

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ABSTRACT

Platinum/cerium-zirconium-sulfate (Pt/Ce-Zr-SO_4^{2-}) catalysts were prepared by wetness impregnation. Catalytic activities were evaluated from the combustion of propene and CO. Sulfate (SO_4^{2-}) addition improved the catalytic activity significantly. When using Pt/Ce-Zr-SO_4^{2-} with 10 wt% SO_4^{2-}, the temperature for 90% conversion of propene and CO decreased by 75 °C compared with Pt/Ce-Zr. The conversion exceeded 95% at 240 °C even after 0.02% sulfur dioxide poisoning for 20 h. Temperature-programmed desorption of CO and X-ray photoelectron spectroscopy analyses revealed an improvement in Pt dispersion onto the Ce-Zr-SO_4^{2-} support, and the increased number of Pt particles built up more $Pt^{\delta+}$-$(SO_4^{2-})^{\delta-}$ couples, which resulted in excellent activity. The increased total acidity and new Brönsted acid sites on the surface provided the Pt/Ce-Zr-SO_4^{2-} with good sulfur resistance.

1. Introduction

Diesel vehicles are used widely because of their advantages of a high fuel efficiency, reliability, and durability. However, diesel-engine exhaust gases release various hazardous pollutants, such as carbon monoxide (CO), hydrocarbons (HC), nitrogen oxides (NO_x), particulate matter, and sulfur dioxide (SO_2). These substances are major sources of air pollution, such as haze fog, and are a threat to human and environmental health. Hence, regulations on exhaust-gas emissions from automotives are becoming stricter [1–5]. Diesel-vehicle catalyst systems that consist of diesel-oxidation catalysts (DOCs) [1,2], diesel particulate filters [6,7], and nitrous-oxide (NO_x) selective reduction catalysts (SCRs) [8,9] have been developed. These catalysts have been studied extensively to improve their activity and stability. DOCs have been used to convert unburned CO and hydrocarbons to carbon dioxide and water [10–13]. DOCs can also oxidize nitrogen monoxide to nitrogen dioxide, which is beneficial for de-NO_x activity of the fast SCR reaction and the oxidation of soot collected by the diesel particulate filters downstream [14,15].

Pt-based diesel-oxidation catalysts are used widely in DOC systems because of their high catalytic activity [16–18]. Ceria-zirconia solid solution is used as an excellent support because it combines a high oxygen storage/release capacity from the surface redox cycle Ce^{4+}/Ce^{3+}, and fine thermal stability caused by zirconium(IV) (Zr^{4+}) doping into the CeO_2 lattice [19]. A high dispersion of precious metal-like platinum is maintained by strong interaction of platinum-oxygen-cerium (Pt-O-Ce), which is termed the “anchor effect” [20]. However,

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DOC catalysts are problematic in that the catalysts operate at low temperatures because the diesel exhaust gas temperature is significantly lower than that of the gasoline exhaust and is deactivated in the presence of SO_2 [21,22]. Consequently, oxidation catalysts are required urgently to improve the low-temperature activity and sulfur poisoning resistance in DOC systems.

Acidic oxide addition (such as sulfate) [23–27] can improve the low-temperature oxidation activity of catalysts remarkably. Gu et al. [23] showed that SO_2 pretreatment on cerium(IV) oxide (CeO_2) could result in an enrichment of Ce^{3+} on the sample surface, which leads to an increased content of active surface oxygen and strong-acid site production in the sample; these effects benefit SCR activity. Rivas et al. [24] reported that DCE-removal temperatures are lowered considerably by 80 °C (temperature for 50% reactant conversion, T_{50}) and 120 °C (temperature for 90% conversion, T_{90}) over a sulfated $Ce_{0.5}Zr_{0.5}O_2$ catalyst, which is associated with an increased total acidity and new Brönsted acid sites. Burch et al. [25] and Corro et al. [26] reported that the propane oxidation activity of Pt/Al_2O_3 was promoted by presulfation, and they ascribed this response to the interaction of surface sulfates with highly oxidized surface Pt atoms at the edge of the Pt particles. The effects of sulfation on the state of Pt that is supported on ceria-zirconia mixed oxides and the activity for hydrocarbon oxidation were also investigated. Weng's group [28,29] proposed that some more active sites are generated at the platinum-sulfate interface.

Several mechanisms for sulfur deactivation have been summarized in the literature [30–32], including: (1) a Pt crystal structure rearrangement, (2) electronic effects caused by sulfur, (3) the formation of surface Pt sulfate, (4) the formation of sulfate on the support or Pt/support interface, and (5) modification of Pt-CO bonding. According to Datta et al. [33], SO_2 adsorption onto γ-Al_2O_3 occurs initially at Lewis acid sites. Hamzehlouyan et al. [22] observed that Pt promotes surface sulfate formation, and thereby blocks sites where carbon monoxide is adsorbed preferentially. However, these processes require direct Pt-catalyst treatment in a SO_2 atmosphere, and research on support sulfation effect on Pt-based catalysts is limited.

This work focuses on the support sulfation (Ce-Zr-SO_4^{2-}) effect and aims to investigate the effect of SO_4^{2-} on the low-temperature catalytic activity of Pt/Ce-Zr-SO_4^{2-} and evaluate the effect of support sulfation on the SO_2-poisoning resistance.

2. Experimental

2.1. Catalyst preparation

A Ce-Zr support with a cerium to zirconium mole ratio of 4:1 was prepared by co-precipitation. Cerium(III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) and zirconium nitrate trihydrate ($Zr(NO_3)_4{\cdot}3H_2O$) were dissolved in deionized water. An excess NaOH solution (1 mol/L) was added slowly while stirring via a peristaltic pump to the Ce-Zr solution. The pH was adjusted to above 10. The precipitate was centrifuged, washed, filtered, dried overnight at 110 °C, and calcined at 500 °C for 3 h. The synthesized sample was labeled CZ.

Ce-Zr-SO_4^{2-} supports different sulfuric acid mass fractions (0.5, 5, 10, and 15) wt% by wetness impregnation using an aqueous solution of sulfuric acid (H_2SO_4). CZs (3 g) were added into the mixture of H_2SO_4 solution (0.1 mol/L; 1.5, 15, 30, and 45 mL) and deionized water (48.5, 35, 20, and 5 mL). These solutions were impregnated uniformly by slow removal of water using a rotary evaporator at 70 °C. The resulting samples were dried overnight at 110 °C, calcined at 500 °C for 3 h, and labeled CZ-*x*S, where *x* represents the mass percentage of sulfate over the support.

The CZ-*x*S were loaded with 1 wt% Pt by wetness impregnation and water removal by using a rotary evaporator at 70 °C, in which chloroplatinic acid (H_2PtCl_6) solution was used as a Pt precursor. The catalysts were dried at 110 °C and calcined at 500 °C for 3 h. Finally, Pt/CZ, Pt/CZ-0.5S, Pt/CZ-5S, Pt/CZ-10S, and Pt/CZ-15S were obtained.

Pt/CZ-*x*S-B (*x* = 0.5, 5, 10, 15; B = sulfate loaded behind Pt) were prepared by using the same process as that for CZ-*x*S, except that Pt/CZ was used instead of CZ.

2.2. Characterization

Specific surface areas of catalysts were measured using the Brunauer-Emmett-Teller (BET) method from nitrogen adsorption isotherms. Experiments were conducted on an ASAP 2020 instrument (Micromeritics) at –196 °C. Prior to the experiments, samples were degassed at 200 °C for 4 h.

X-ray diffraction (XRD) patterns of the samples were recorded on an X' Pert Pro diffractometer with Cu K_α (λ = 0.154056 nm, 40 kV, 30 mA) radiation. The measurements were conducted in the 2θ range of 10° to 100° with a step size of 0.033°.

Temperature-programmed reduction with hydrogen (H_2-TPR) was performed on a FINE SORB-3010 E instrument. The sample (200 mg) was placed in a quartz reactor, pretreated in highly pure Ar at 200 °C for 2 h, and then cooled to 60 °C. The reducing gas used in all experiments was 5% H_2/95% Ar. The temperature was increased from 60 °C to 900 °C at 10 °C/min. The flow rates were 30 mL/min. A TCD detector was used at the reactor outlet to measure the hydrogen volume that was consumed during reduction.

Temperature-programmed desorption of CO (CO-TPD) was investigated on a FINE SORB-3010 E instrument. The sample (100 mg) was placed in a quartz reactor, pretreated in 5% H_2/Ar at 300 °C for 1 h, and then cooled to 30 °C in a He flow. CO adsorption was performed by admitting a flow of 5% CO/95% N_2 at 30 °C for 1.5 h. The sample was exposed to He for 1 h at 100 °C to remove reversibly and physically bound CO from the surface. Finally, desorption was carried out from 100 °C to 500 °C at 5 °C/min in a He stream. The flow rates were 30 mL/min. A TCD detector was used at the reactor outlet to measure the CO volume during desorption.

Temperature-programmed desorption of ammonia (NH_3-TPD) was conducted on a FINE SORB-3010E instrument. The sample (100 mg) was placed in a quartz reactor, pretreated in