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Effect of active oxygen on the performance of Pt/CeO_2 catalysts for CO oxidation☆

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ABSTRACT

This study was focused on the influence of active oxygen on the performance of Pt/CeO_2 catalysts for CO oxidation. A series of CeO_2 supports with different contents of active oxygen were obtained by adding surfactant at different synthesis steps. 0.25 wt% Pt was loaded on these CeO_2 supports by incipient-wetness impregnation methods. The catalysts were characterized by N_2 adsorption, X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM), H_2 temperature-programmed reduction (H_2-TPR), dynamic oxygen storage capacity (DOSC) and *in-situ* DRIFTS technologies. For S-f supports, the surfactant was added into the solution before spray-drying in the synthesis process, which facilitates more active oxygen formation on the surface of CeO_2. After loading Pt, the more active oxygen on CeO_2 contributes to dispersing Pt species and enhancing the CO oxidation activity. As for the aged samples, Pt-R-h shows the highest activity above 190 °C because of the presence of more partly oxidized $Pt^{\delta+}$ species. Thus the activity is also influenced by the states of Pt and the $Pt^{\delta+}$ species may contribute to the high activity at elevated temperature.

1. Introduction

Supported precious metal catalysts with high activity and selectivity are extensively used in the air pollution control.[1–3] For instance, precious metal supported on alumina has been widely researched and applied in NO_x storage and reduction, diesel oxidation catalysts.[2–5] Compared with the alumina supports, CeO_2 is an excellent redox support that can greatly enhance the reaction rates involving redox steps, such as CO oxidation reaction, where it can act as an oxygen buffer.[6,7] Because of the unique oxygen storage capacity (OSC) and redox properties induced by the reversible Ce^{4+}/Ce^{3+} redox cycles, CeO_2 is widely used in automotive exhaust treatment catalysts.[3,7–10]

Pt/CeO_2 has attracted more attention because of its highly enhanced catalytic performance and wide range of applications, such as water gas shift,[9,11] CO oxidation,[12–14] methane partial oxidation.[15,16] Therefore, the interaction between Pt and CeO_2 supports has been widely investigated. As reported in the literature,[17] the interaction mainly involves the transfer of electron from Pt to CeO_2 and oxygen spillover from CeO_2 to Pt at Pt–CeO_2 interface. Meanwhile, the presence of Pt can change the surface properties of CeO_2 by weakening the Ce–O bond, which makes the surface CeO_2 more reducible.[18] Besides the Pt–O–Ce bonding formed at the interface can effectively inhibit the Pt migration and sintering at elevated temperature,[19,20] which is absent on Pt/Al_2O_3[21] and Pt/ZrO_2[22] catalysts. Recently, it is reported that the morphology of CeO_2 also has an effect on the interaction with Pt. Meher et al reported that suitable surface morphologies of CeO_2 which possess higher number of oxygen vacancies can effectively facilitate ideal Pt crystal growth and enhance the Pt dispersion.[13] Besides, Yang et al reported that the structure of Pt is affected by the morphology of CeO_2 and the Pt/CeO_2 nanorods showed much higher CO oxidation activity because of the higher concentration of oxygen vacancies in CeO_2 nanorods.[23] These researches mainly focused on the influence of oxygen vacancies on the interaction

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between Pt and CeO_2. However, the effect of active oxygen on the performance of Pt/CeO_2 catalysts is rarely investigated. It is noteworthy that the active oxygen of CeO_2 directly determines the OSC, which contributes to increasing the oxidation reaction rates. Therefore, the active oxygen is also one of the most important factors that influence the catalytic performance of Pt/CeO_2 catalysts.

In this work, we systematically investigated the effect of active oxygen on the performance of Pt/CeO_2 catalysts for CO oxidation reaction. CeO_2 supports with different contents of active oxygen were prepared by adding surfactant at different synthesis steps. N_2 adsorption was employed to characterize the physical structure. H_2-TPR and DOSC measurements were performed to investigate active oxygen species and the rates of oxygen release. CO chemisorption was carried out to analyze the Pt dispersion. *In-situ* CO-DRIFTS was employed for semi-quantitative analysis of the relative amounts of different Pt species.

2. Experimental

2.1. Catalyst preparation

The CeO_2 supports were prepared by precipitation method. $Ce(NO_3)_3 \cdot 6H_2O$ solution (1.5 mol/L) was dropped into ammonia precipitator under vigorous stirring at 30 °C. The precipitates were stirred for 3 h with air bubbled into the reactor until the Ce^{3+} was oxidized completely. Then the solution was crystallized at 90 °C for 6 h. After filtered and washed by de-ionized water, the products were dissolved in de-ionized water and dried through air-blast spray-drying process. Finally, the powders of CeO_2 were obtained after calcination at 500 °C for 3 h. Note that the surfactants PEG-4000 and 6-aminocaoroic acid were added into the solution before reaction, crystallization and spray-drying, respectively, to obtain different surface chemical states. The synthesized samples were named as R-f, C-f, S-f, respectively. Among these samples, the "R" is short for "reaction"; the "C" is short for "crystallization"; the "S" is short for "spray-drying", and the "f" represents fresh samples.

0.25 wt% Pt was loaded on the series of fresh CeO_2 supports by incipient wetness impregnation using $Pt(NO_3)_2$ solution. The impregnated materials were dried in air overnight at 100 °C and subsequently calcinated in air at 500 °C for 3 h to get the as-prepared fresh Pt/CeO_2 samples, noted as Pt-R-f, Pt-C-f, Pt-S-f, respectively. Then all samples were aged at 750 °C in 10% H_2O/air for 20 h to get the aged samples and named as Pt-R-h, Pt-C-h, Pt-S-h, respectively. The "h" represents aged samples.

2.2. Catalyst characterization

The specific surface area and pore structure were measured by N_2 adsorption at 77 K with an ASAP 2460 Micromeritics apparatus. Prior to the measurement, samples were degassed at 300 °C under vacuum for 5 h to eliminate the adsorbed gases.

X-ray diffraction (XRD) patterns were recorded from 20° to 65° with a 0.01° step size using a Bruker D8 Focus equipped with nickel-filtered Cu Kα radiation ($\lambda = 0.154056$ nm). The Pt loading was analyzed from inductively coupled plasma (ICP) and carried out on an Agilent 5100 ICP–OES.

High-resolution transmission electron microscopy (HRTEM) was performed using an FEI Tecnai G2 F20 microscope with a field-emission gun operated at 200 kV. Prior to imaging, the samples were dissolved in anhydrous ethanol and dropped onto 230 mesh Cu grids coated with ultrathin carbon, then dried in air overnight.

CO chemisorption was conducted on a Micromeritics AutoChem II 2920 instrument. Prior to the experiment, a series of pretreatments were performed as the literature[24] suggested. Firstly, the samples were oxidized (20% O_2/N_2) at 500 °C for 30 min and reduced (5% H_2/N_2) at 350 °C for 10 min. In order to block the CO adsorption on the surface site of CeO_2, a CO_2 pretreatment (10% CO_2/N_2) was performed after the samples were cooled down to room temperature under N_2 atmosphere. Then, 15 times CO pulse (15 s) and N_2 (45 s) purge were introduced after reduction process under 10% H_2/N_2 for 10 min.[25] The dispersion of Pt was calculated based on the assumption that CO: $Pt_{surface} = 1{:}1$.[26]

Temperature-programmed reduction by hydrogen (H_2-TPR) experiment was conducted on PX200 catalyst characterization instrument equipped with a thermal conductivity detector (TCD) to characterize the reducibility of catalysts. The samples were pretreated at 500 °C under 5% O_2/N_2 (30 mL/min) for 30 min, then cooled down to 30 °C under N_2 purging. The samples were heated at a rate of 10 ℃/min from 30 to 900 °C under a flow of 5% H_2/N_2 (20 mL/min).

Dynamic oxygen storage capacity (DOSC) test was performed on a self-designed assessing instrument, monitored online by a Hidden HPR20 quadruple mass spectrometer. 25 mg sample diluted with 40 mg quartz sand was placed in the quartz tube reactor. Briefly, CO (4% CO/1% Ar/He) and O_2 (2% O_2/1% Ar/He) were pulsed alternately with a frequency of 0.1 Hz at 300–500 °C. The detailed experimental process was described in our previous work.[27] The DOSC was calculated by integrating the generated CO_2 during one CO–O_2 cycle.

In-situ diffuse reflectance infrared Fourier transform spectroscopy (*in-situ* DRIFTS) spectra were recorded on a Nicolet 6700 FTIR spectrometer equipped with a MCT detector. ZnSe window was applied on a commercial high-temperature chamber (PIKE). The samples were initially pre-treated at 500 °C under 20% O_2/N_2 for 30 min, then cooled down to 350 °C and reduced by 5% H_2/N_2 for 10 min, which is in accordance with the CO oxidation activity tests. When the samples were cooled down to 30 °C under N_2 purging, 2% CO/N_2 was flowed in for 30 min. After that, the samples were purged with N_2 again to eliminate the CO with physical absorption and the spectrum was collected until there was no change. Besides, the spectrum under CO oxidation condition was collected to investigate the variation of Pt states. After pre-treatment, the samples were heated from 100 °C to 500 °C at 10 ℃/min under reactant gas.

2.3. Catalyst activity measurement

The CO oxidation activity was carried out with a fixed-bed continuous flow reactor. The catalysts (0.1 g catalysts mixed with 1.9 g quartz sands) were held in a quartz tube by packing quartz wool at both ends of the catalysts bed. The samples were pretreated at 500 °C under 20% O_2/N_2 for 30 min, then followed with a pre-reduction under 5% H_2/N_2 for 10 min at 350 °C. Subsequently, the sample was heated from 100 to 500 °C at 10 ℃/min under reactant gas: 1000 ppm CO, 5% O_2, N_2 as balance with a gas hourly space velocity (GHSV) of 72,000 h^{-1}. The total flow was 1 L/min. The outlet concentrations were analyzed by an on-line Fourier transform infrared spectrometer (MKS-2030). The rates of CO oxidation based on Pt loading were calculated using the following equations:

$$X_{CO}\ (\%) = \frac{CO_{inlet} - CO_{outlet}}{CO_{inlet}} \times 100\% \tag{1}$$

$$\text{Rates} \ = \frac{X_{CO}[\%] \times F_{CO}[\mathrm{L/min}] \times 195.1[\mathrm{g/mol}]}{m_{catal}[\mathrm{g}] \times \omega_{Pt}[\%] \times 60[\mathrm{s/min}] \times 22.4[\mathrm{L/mol}]} \tag{2}$$

Here, X_{CO} is conversion of CO, F_{CO} volumetric flow rate of CO, m_{catal} mass of catalysts, ω_{Pt} the mass fraction of Pt in Pt/CeO_2 catalysts.