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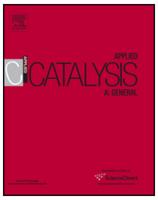

Feature Article

A highly effective catalyst of Co-CeO_2 for the oxidation of diesel soot: The excellent NO oxidation activity and NO_x storage capacity

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ABSTRACT

In the catalytic combustion of diesel soot, the role of NO in the exhaust emission and the simultaneous reduction of NO by soot are two fascinating problems. Herein, the Co-CeO_2 catalyst prepared by the citrate acid sol-gel method was developed to catalyze the NO_x-assisted soot oxidation. The effect of the Co amount on the physicochemical and catalytic properties of the Co-CeO_2 catalysts was investigated in detail. When the molar ratio of Co/Ce was 50/50, the $Co_{50}Ce_{50}$ mixed oxide catalyst exhibited the lowest soot oxidation temperature (T_m of 335 °C) in the feed gas of NO + O_2, and the presence of water can improve obviously the catalytic combustion of soot with T_m of 310 °C. The presence of Co can improve the reduction of surface oxygen of ceria, and Ce can promote the reduction of Co_3O_4 to CoO, resulting in the enhancement of the catalytic activity of Co-CeO_2 for NO oxidation and its capacity for NO_2 storage as the surface nitrates. The soot oxidation on the Co-CeO_2 catalyst can be promoted by "NO_2-assistance": the nitrate species are preferentially formed on the Co active sites and stored on the catalyst surface, and then NO_2 produced by NO oxidation and the decomposition of nitrate stored on the surface at lower temperature, reacts with soot. That is, the stored NO_x species initiates the beginning of soot oxidation, and the NO oxidation ability of the catalyst is responsible for the extensive soot oxidation by NO + O_2, in which NO is reduced by carbon in soot combustion. The combination of high NO oxidation activity and high NO_2 storage capacity makes the $Co_{50}Ce_{50}$ oxide catalyst as an efficient catalyst for the NO_x-assisted soot oxidation.

1. Introduction

Soot particles are formed as undesired by-products in the combustion processes, and one of the main pollutants emitted by the diesel engines together with NO_x, CO and unburned hydrocarbons [1], which seriously damage to the human health. The diesel particle traps with different designs can be used for soot removal from gas streams, in which the wall-flow monoliths is the most popular [2,3]. Once soot is collected on a filter, the different regeneration strategies can be applied. The thermal combustion of diesel soot usually needs higher temperature, such as above 450 °C, and the catalysts play a key role in the combustion of soot at lower ignition temperature [4].

In recent years, the several catalysts were synthesized and applied in the soot oxidation by O_2 and/or NO_x. Compared with the precious metal catalysts, the low-cost metal oxides are widely accepted to be an alternative. The transition metal oxide Co_3O_4 is considered to be a typical oxidation catalyst, and often used in the low-temperature CO oxidation [5,6], propane oxidation [7], methanol oxidation [8] and so forth, and applied as the catalyst for N_2O decomposition [9,10]. As is well-known, Co_3O_4 has a spinel structure with Co^{2+} and Co^{3+} located at the tetrahedral and octahedral sites. In the oxidation reaction, Co^{3+} played more important role than Co^{2+}, and the redox ability of Co^{3+} has a great influence on its catalytic activity [6]. And the high activity of Co_3O_4 is likely related to the high reactivity of the active oxygen species, due to the weakening of the Co-O bond strength [11,12], which can be further improved by adding promotional component.

Cerium is the very important one of rare earth elements, and used widely as the catalyst or carrier ceria in many chemical reactions, because of its charming capacity to store and release oxygen by the redox cycle of Ce^{4+} and Ce^{3+} [13]. Based on the chemical characteristics of ceria, the ceria-based materials exhibited the highly catalytic activity for the diesel soot combustion [14–17]. Thus, the combination of cobalt oxide and ceria to form Co-Ce mixed oxide arose our great interest for the diesel soot combustion

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[18], which was utilized as the catalyst in several chemical processes, e.g. methane emission abatement [19], low-temperature CO oxidation [20,21] and toluene oxidation [22]. Dhakad et al. found that Co_3O_4-CeO_2 mixed oxide prepared by the co-precipitation method exhibited the excellent catalytic activity and good thermal stability for diesel soot oxidation, which is attributed to the promotional effects of an optimum amount of cobalt oxide incorporated in ceria and a small amount of potassium [23]. Liu et al. prepared nanometric CeO_2-supported cobalt oxide materials by the ultrasonic-assisted incipient-wetness impregnation method [24], and found that the Co_{20}/CeO_2 (Co/Ce = 0.2,mol) sample exhibited the best catalytic activity for soot combustion with T_{50} (the reaction temperature of 50% soot oxidation) of 368 °C.

As NO_2 is more active than O_2 in the soot oxidation under NO/O_2 atmosphere and can oxidizes carbon at low temperature [25], the catalytic activities of the soot combustion catalysts were investigated for NO oxidation to NO_2 as well [26]. Jelles et al. [27] studied the influence of NO_x on the oxidation of metal activated soot combustion and proposed the oxidation mechanism, and thought that the metal catalyst can maintain an oxidation cycle of NO to NO_2 that results in high soot oxidation rates, in which NO_2 plays an important role. The $CoAl_2O_4$ spinel catalyst showed the high activity for the soot combustion, which was attributed to its high NO_x chemisorption capacity and catalytic activity for the NO oxidation to NO_2 [28]. The effect of the NO presence on the soot combustion over ceria/zirconia based catalysts was investigated. Over the CZKRu catalyst, the presence of NO promoted soot oxidation, where the occurrence of the oxidation/recycling NO to NO_2 was in favor of soot combustion, and the presence of ruthenium increased the formation of surface oxygen complexes thus favoring the carbon-NO_2-O_2 oxidation [29]. In the NO_2-assisted soot oxidation over the ceria catalysts, NO can be oxidized to NO_2 then the NO_2-soot reaction yields NO again, such the recycling of NO is important for the efficiency of ceria catalysts [30]. However, the catalytic activities of these catalysts above for carbon oxidation still needs to be improved, and the NO_x role should also be further clarified when the catalyst and soot are mixed with different contact modes. It is interesting whether in the soot combustion NOx can be reduced by soot or other carbon-including particles.

Based on the Co_3O_4-CeO_2 catalyst has the high catalytic activity for NO oxidation [31], the Co-modified CeO_2 catalyst were prepared by the citrate acid sol-gel method, and used in the NO_x-assisted soot oxidation. The effect of the Co amount on the physicochemical and catalytic properties of Co-CeO_2 was investigated, and its catalytic activity for NO oxidation and NO_x storage capacity were studied. *In situ* DRIFT spectroscopy was used to test the catalytic oxidation of the soot-catalyst mixture in the presence of NO + O_2. Based on these research results, the mechanism of NO_x-assisted soot oxidation over the Co-CeO_2 catalyst was discussed, and an important result was obtained: the combination of high NO oxidation activity and high NO_2 storage capacity makes Co-CeO_2 be a high-efficient catalyst for NO_x-assisted soot oxidation.

2. Experimental section

2.1. Catalyst preparation

Co_3O_4-CeO_2 mixed oxide was prepared by the sol-gel method. An appropriate amount of $Co(NO_3)_2{\cdot}6H_2O$ and $Ce(NO_3)_3$ were dissolved in de-ionized water. Citric acid was added as the complexing agent with the molar ratio of citric acid/Co of 1.3. The mixed aqueous solution was evaporated under stirring until the transparent gel was formed. It was dried at 120 °C overnight. Finally, the obtained solid was calcined at 500 °C for 3 h. In the Co_xCe_y mixed oxide samples, x + y was equal to 100% (mol). Pure Co_3O_4 and CeO_2 were also prepared by this sol-gel method.

2.2. Catalytic combustion of soot

The activity of the catalyst for the soot combustion was tested in a fixed bed micro-reactor (Φ6 mm × 300 mm) at atmosphere pressure and the temperature-programmed (TP) way. Commercial carbon black (Degussa Printex-U, 97.23 wt.% C, 0.73 wt.% H, 1.16 wt.% O, 0.19 wt.% N, 0.45 wt.% S) was used as a model soot. The soot-catalyst mixture consisted of 5 mg soot and 45 mg catalyst was milled in the agate mortar for “tight contact”, and mixed by a spatula for “loose contact”, and then the sample was diluted by 200 mg SiO_2 particles to reduce the pressure drop and to prevent thermal runaway. The reactant gas was consisted of 500 ppm NO + 5% O_2/Ar with 200 mL/min. The TP-soot combustion was carried out at 10 °C/min from 50 to 600 °C. The concentrations of CO_2 and CO in outlet gas were analyzed after methanation on line by a gas chromatograph with the FID detector. NO, NO_2 and NO_x (NO + NO_2) concentrations in outlet gas were detected online by a NO_x analyzer (Thermo, Model 42i-LS).

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of samples were recorded on a Bruker D8 powder diffractometer with CuKα radiation operated at 40 kV and 40 mA, in which the 2θ step size was 0.02° and the scanning speed was 6°/min. The N_2 adsorption/desorption experiments were carried out at −196 °C on a Micromeritics ASAP 2020 Sorptometer, and the specific surface area of the catalyst was calculated by the BET equation.

Hydrogen temperature-programmed reduction (H_2-TPR) was performed on a PX200 apparatus (Tianjin Pengxiang Technology Co. Ltd.). 50 mg catalyst was loaded in U-type quartz tube reactor (Φ10 mm), and was heated in the flow of 5 vol.% H_2/N_2 (40 mL/min) at 10 °C/min from 100 to 800 °C. The amount of H_2 uptake was measured by thermal conductivity detector (TCD).

NO temperature-programmed oxidation (NO-TPO) was performed in a fixed bed micro-reactor system with the NO_x analyzer (Thermo, Model 42i-LS). 100 mg catalyst was used. The temperature program, reactant gas and others were the same as the catalytic activity evaluation described above.

NO temperature-programmed desorption (NO-TPD) was performed in a fixed bed micro-reactor system with the NO_x analyzer. 100 mg catalyst was used and treated at 350 °C for 30 min in the mixed gas of 500 ppm NO + 5%O_2/Ar (200 mL/min). After being cooled to room temperature, the reactor was swept with pure Ar until no NO_x was detected. Then, TPD was run in the Ar flow of 200 mL/min at 10 °C/min from room temperature to 600 °C. The adsorption amount of NO_x was measured by the NO_x analyzer.

In situ diffuse reflection infrared Fourier transform spectroscopy (DRIFTS) spectra on the soot-catalyst mixture in the mixed gas of 500ppmNO + 5%O_2/Ar were obtained on a Nicolet NEXUS 670 FT-IR spectrometer equipped with an *in situ* diffuse reflection chamber and a high sensitivity MCT detector. Prior to collecting the spectra, the soot-catalyst (1:9) mixture was milled in an agate mortar for “tight contact”, and then the sample was pretreated in the Ar flow at 500 °C for 30 min. During the cooling, background spectra were collected at 500, 400, 300, 200 and 100 °C in the Ar flow. After being cooling to 100 °C, the mixed gas of 500ppmNO + 5%O_2/Ar was flowed through the sample chamber at 50 mL/min. The DRIFTS spectra were taken down as a function of time at designated temperatures, and saved in Kubelka-Munk unit with a resolution of 4 cm^{-1} and 64 scans.