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Article

Active oxygen-assisted NO-NO₂ recycling and decomposition of surface oxygenated species on diesel soot with Pt/Ce_{0.6}Zr_{0.4}O₂ catalyst

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ARTICLE INFO

Article history:

Received 9 November 2013

Accepted 13 December 2013

Published 20 March 2014

Keywords:

Platinum-based catalyst

Ceria-zirconia mixed oxide

Soot oxidation

Nitrogen monoxide-nitrogen dioxide recycling

Surface oxygenated species

ABSTRACT

A Pt/Ce_{0.6}Zr_{0.4}O₂ catalyst was synthesized by impregnating a Ce_{0.6}Zr_{0.4}O₂ support with Pt(NO₃)₂ solution. This material exhibits higher catalytic activity than Pt/Al₂O₃ for soot oxidation under loose contact conditions in both NO + O₂ and O₂ atmospheres. The results show that the pronounced activity of this catalyst is attributed to a synergistic effect arising from the combination of Pt and Ce_{0.6}Zr_{0.4}O₂ solid solution, leading to a remarkable increase in the availability of active oxygen at temperatures as low as 450 °C. The NO↔NO₂ recycling efficiency is improved over Pt/Ce_{0.6}Zr_{0.4}O₂ catalyst, enhancing the ability of the NO₂-soot reaction to generate surface oxygenated complexes (SOCs) on the soot. More importantly, the catalytic oxidation of these SOCs can be accelerated with the participation of active oxygen from the CeO₂-ZrO₂ solid solution. As a result, during soot oxidation under NO + O₂, the light-off temperature of the Pt/Ce_{0.6}Zr_{0.4}O₂ catalyst is lowered by 34 °C than that of Pt/Al₂O₃ catalyst.

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1. Introduction

Owing to the environmental and health impacts of diesel particulate matter (PM) and the necessity of complying with increasingly stringent automobile emissions regulations, efforts to reduce PM emissions are ongoing, even though achieving such reductions remains challenging. PM is primarily composed of carbonaceous particles (often called soot) originating from incomplete in-cylinder oxidation of the fuel, with diameters ranging from a few nanometers (10–20 nm) to several hundred nanometers [1,2]. Trapping PM on a filter followed by oxidation is an efficient means of eliminating this pollutant and, with the help of catalysts, the temperature required for the oxidation of soot (normally > 600 °C) can be significantly reduced. Under the conditions that typically occur in an actual

catalytic diesel particulate filter (DPF), however, good contact between the PM and the catalyst is very difficult to obtain; the loose contact obtained by mixing soot and catalyst by hand has been reported to be comparable to the degree of contact obtained in a DPF [3]. Under such loose contact conditions, the majority of the carbon atoms are in contact with the surrounding gaseous phase and, consequently, the soot oxidation temperature can be significantly reduced due to the NO₂ produced over the catalyst [1,2]. For this reason, the redox properties of the Ce^{3+/4+} couple and the capacity of CeO₂ to exchange oxygen with the gas phase make CeO₂-based materials one of the most promising soot combustion catalysts.

It has been reported that CeO₂-based catalysts, in addition to promoting NO₂-assisted soot combustion, also allow active oxygen-assisted reactions even in the loose contact mode [4–7].

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This work was supported by the National Natural Science Foundation of China (51072096), the National Basic Research Program of China (973 Program, 2010CB732304), and the National High Technology Research and Development Program of China (863 Program, 2013AA065302).

DOI: 10.1016/S1872-2067(14)60004-8 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 35, No. 3, March 2014

In this process, active oxygen species are generated when lattice oxygen from CeO_2 is replaced by gas phase oxygen [8,9]. In the presence of NO_x , the desorption of stored oxygen generated by the NO_2 - CeO_2 reaction may also produce active oxygen species which can be transferred to the soot surface to accelerate the oxidation [4,7]. Compared with pure CeO_2 , CeO_2 - ZrO_2 mixed oxides exhibit better oxygen storage capability as well as enhanced stability during sintering, and thus $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ solid solutions have become one of the key components in auto exhaust treatment catalysts [10]. The synergistic effect between Pt and CeO_2 - ZrO_2 may further improve the catalytic performance, since the Pt can accelerate the mobility of the active oxygen in the CeO_2 - ZrO_2 [6,10]. As such, it is reasonable to suggest that Pt/ CeO_2 - ZrO_2 catalysts have potential application to the oxidation of soot and may be helpful based on the ongoing trend in which increasingly significant restrictions are imposed on diesel NO_x emissions [5,11].

Past studies have examined the applicability of CeO_2 -based catalysts to the soot oxidation reaction and have focused on the generation of active oxygen and the subsequent reaction promotion effect [4–7], but have lacked a fundamental understanding of the manner in which the active oxygen reacts with soot, especially in the presence of NO_x . The proposed reaction mechanisms have been based purely on speculation and little direct evidence has been presented. In this work, a systematic comparison between Pt/ Al_2O_3 catalyst with Pt/ CeO_2 - ZrO_2 catalyst was carried out to explore the reaction pathways on these catalysts in the presence and absence of NO_x . Efforts were made to obtain a clear insight into the roles of active oxygen in the generation and decomposition of surface oxygenated complexes on soot over Pt/ CeO_2 - ZrO_2 catalyst.

2. Experimental

2.1. Materials

$\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ (CeZr) mixed oxides were synthesized using a citric-aided sol-gel method. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99%, Rongruida, China) and $\text{ZrO}(\text{NO}_3)_2 \cdot 5\text{H}_2\text{O}$ (99%, Rongruida, China) were used as the precursors while citric acid (99%, Yili, China) and polyglycol (20000 $\pm$ 200 g/mol, Yili, China) were used as complexing agents. A mixture of the precursor salts, citric acid, polyglycol, and deionized water at a molar ratio of 1:2:0.2:100 was stirred at 90 °C until a spongy yellow gel was formed. This gel was dried overnight at 110 °C and then calcined at 700 °C for 3 h in a muffle furnace. For reference, a sample of pure Al_2O_3 was also subjected to the same calcination process.

A solution of $\text{Pt}(\text{NO}_3)_2$ (27.82 wt%, Heraeus, Germany) was added to $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ or Al_2O_3 in such a manner as to ensure Pt loadings are 1%. After impregnation, the catalysts were dried at 110 °C for 12 h and calcined at 500 °C for 2 h in static air. According to a previous study, 100% of the added Pt should be present on the supports as various Pt species [6]. The resulting catalysts were denoted as PtCeZr and PtAl, respectively.

Printex-U (Degussa, Germany) was used as a model soot. It had an average particle size of 25 nm and a specific surface area of 100 m^2/g . Samples of NO_2 -treated soot (Nsoot) con-

taining various surface oxygen complexes were obtained by treating the Printex-U with NO_2 (500 ppm) in 10% O_2/N_2 flowing (200 ml/min) at 350 °C for 4 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of various samples were acquired using a diffractometer (D8 ADVANCE, Bruker, Germany) employing Cu K_α radiation ($\lambda = 0.15418$ nm) and operating at 40 kV and 30 mA. The XRD patterns were recorded at 0.02° intervals over the range of $2\theta = 20^\circ$ – 80° at a scanning velocity of 4°/min.

The specific surface areas of the samples were obtained from N_2 adsorption-desorption isotherms at -196 °C by the four-point BET method, using an automatic surface analyzer (F-Sorb 3400, Gold APP Instrument, China). The samples were degassed at 200 °C for 2 h prior to the measurements.

Pt dispersion on each of the catalysts was assessed using a Micromeritics AutoChem II 2920 apparatus with a thermal conductivity detector (TCD). During each experiment, approximately 50 mg of catalyst was placed in a U-shaped quartz tube ($\phi 10$ mm) and reduced under a flow of 10% H_2/Ar (50 ml/min) while raising the temperature up to 400 °C at a rate of 10 °C/min, and then held at 400 °C for 30 min under a He flow (50 ml/min) to allow proper degassing. The sample was subsequently cooled to 25 °C and a loop gas consisting of 10% CO/He (20 ml/min) was introduced to the sample in pulses while the TCD signal was recorded until the peak area became constant. The percent dispersion was calculated by dividing the numbers of exposed surface Pt atoms (as determined by CO chemisorption) by the total amount of Pt in the catalyst. The mean Pt particle size was determined from CO chemisorption data by assuming all surface Pt particles were spherical in shape.

Transmission electron microscope (TEM) images were acquired using an FEI Tecnai G2 20 with an acceleration voltage of 200 kV. The size distribution of the Pt crystallites was determined by measuring 100 particles in each sample.

Infrared (IR) spectra of CO adsorbed on the samples were recorded on a Nicolet 6700 FTIR spectrometer equipped with an MCT detector. During this process, the samples were first pretreated under N_2 (50 ml/min) at 500 °C for 30 min then cooled to RT, following which spectra were obtained after exposing the catalyst to 1% CO/N_2 (50 ml/min) for 30 min followed by purging with N_2 .

H_2 temperature-programmed reduction (H_2 -TPR) was performed using a Micromeritics AutoChem II 2920. Prior to measurements, 50 mg of each sample was pretreated under a flow of 10% O_2/He (50 ml/min) at 300 °C for 30 min to allow proper degassing and then cooled to RT and flushed for 10 min. Finally, the treatment gas was switched to 10% H_2/Ar (50 ml/min) and the reactor temperature was raised to 800 °C at a rate of 10 °C/min. H_2 consumption was monitored by TCD.

The oxygen storage capacity (OSC) of the catalysts was measured using a flow reactor system equipped with solenoid valves, determining the composition of the effluent gases with an online mass spectrometer (Omnistar 200). Typically, 25 mg

of sample was preheated under a flow of 2% O₂/He (300 ml/min) prior to performing trials at 450 °C. The dynamic oxygen storage capacity (DOSC) of samples was measured by alternating CO and O₂ pulses every 5 s. The OSC associated with each pulse was calculated as micromoles of CO₂ released per gram of catalyst.

NO temperature-programmed oxidation (TPO) measurements were carried out in a fixed-bed reactor with monitoring the effluent gases by an IR spectrometer (Thermo Nicolet iS10). In these trials, 100 mg of sample was diluted with 300 mg of silica pellets and then sandwiched between portions of quartz wool in a tubular quartz reactor. A gas mixture consisting of NO (1000 ppm) in 10% O₂/N₂ (500 ml/min) was introduced into the tube and the reactor temperature was raised up to 600 °C at 10 °C/min.

Diffuse reflectance IR Fourier transform spectra (DRIFTS) were recorded on the same apparatus used for CO-IR measurements. All samples were first diluted with inert CaF₂, so as to obtain a useable signal-to-noise ratio, at a soot:catalyst:CaF₂ mass ratio of 1:10:100. Samples containing only soot or only catalyst were still diluted with CaF₂ at the same mass ratio. After pretreatment under N₂ (50 ml/min) at 500 °C for 30 min, each sample was cooled to RT and its spectrum was recorded from 100 to 550 °C at 50 °C intervals under various atmospheres. The heating rate applied during these measurements was 10 °C/min.

2.3. Activity measurements

During activity measurements, 10 mg of soot and 100 mg of the catalyst sample were mixed by hand using a spatula for 2 min to obtain “loose contact” conditions. In order to prevent reaction runaway, 110 mg of the soot-catalyst mixture was then diluted with 300 mg of silica pellets. The inlet gas mixture was either NO (1000 ppm) in 10% O₂/N₂ or pure 10% O₂/N₂ at a total flow rate of 500 ml/min, applying a gas hourly space velocity (GHSV) of 30000 h⁻¹. The activity of the catalysts for soot oxidation was evaluated in the same apparatus used for NO-TPO tests and also for TPO reaction at a heating rate of 10 °C/min. In these trials, *T*₅₀ represents the temperature at which 50% of the soot was oxidized. The downstream CO₂/(CO₂ + CO) ratio during soot oxidation was defined as the selectivity for CO₂.

3. Results and discussion

3.1. Catalyst properties

Figure 1 shows the XRD patterns of the catalysts. Both of the CeO₂-ZrO₂-based catalysts exhibit only peaks assigned to the face centered cubic (FCC) fluorite structure of the CeO₂. The diffraction peak at $2\theta = 29.0^\circ$, corresponding to the FCC (111) crystal face, shows a slight shift compared to the same peak in CeO₂, which appears at 28.4° . This effect is primarily due to the substitution of Zr⁴⁺ ions, which have a smaller radius of 0.086 nm, for Ce⁴⁺ ions (0.101 nm) in the fluorite-type ceria lattice, forming a Ce_{0.6}Zr_{0.4}O₂ solid solution which results in lattice

Fig. 1. XRD patterns of CeO₂ (1), CeZr (2), PtCeZr (3), and PtAl (4) samples.

shrinkage [5]. Typical γ -Al₂O₃ peaks are observed in PtAl. No peaks attributed to Pt species are observed for PtCeZr and PtAl samples, indicating that Pt is highly dispersed on both supports. As shown in Table 1, PtAl sample exhibits a much higher specific surface area than the CeO₂-ZrO₂ mixed oxide and the corresponding supported catalyst.

3.2. Pt state

The catalytic oxidation of soot over Pt catalysts is generally believed to depend strongly on the particle size of the Pt particles [12,13]. Since the surface Pt particles on our catalysts were too small to be detected by XRD, CO chemisorption was employed to measure the Pt dispersion. The data in Table 1 demonstrate that a lesser amount of CO is adsorbed on the PtCeZr than that on the PtAl, presumably because of the reduced Pt dispersion on the low surface area CeZr support. To ascertain the Pt particle size distribution on the different catalysts and eliminate the effects of supports on CO chemisorption, high resolution TEM images of the catalysts and the corresponding Pt particle size distributions (PSD) were obtained, as presented in Fig. 2. Here it is evident that the Pt particles on the PtCeZr catalyst are larger than that on the PtAl. The PSD curve obtained with PtAl exhibits a main peak centered at around 1.5 nm, while the PtCeZr exhibits a PSD in which the center of the main maximum peak is shifted to 3 nm. These data are in good agreement with the CO chemisorption results since they indicate that larger Pt particles are formed on the CeZr support.

In addition to the Pt particle size distribution, the oxidation state of the Pt may also affect the activity of the catalysts. Figure 3 presents the IR spectra of CO adsorbed on the catalysts at RT. The PtAl catalyst exhibits three overlapping bands at 2100, 2082, and 2060 cm⁻¹, which are assigned to CO linearly ad-

Table 1

Structural properties of different catalyst samples.

Catalyst	SBET/(m ² /g)	CO/Pt*	Pt dispersion* (%)	Pt diameter* (nm)
PtAl	148	0.82	82	1.4
PtCeZr	10	0.36	36	3.1
CeZr	10	—	—	—

*Obtained from the CO chemisorption results.

Fig. 2. TEM images (a,b) and size distributions (c,d) of Pt particles on PtAl (a,c) and PtCeZr (b,d) catalyst.

sorbed on electron-deficient Pt clusters ($\text{Pt}^{\delta+}$) as well as on the terrace and step sites of Pt^0 crystallites, respectively [14]. In the case of the PtCeZr catalyst, the bands assigned to Pt^0 exhibit dramatically lowered intensity, indicating an obvious decrease in the Pt surface area. These results also correspond nicely with the CO chemisorption results. The band resulting from $\text{Pt}^{\delta+}$ on the PtCeZr (2091 cm^{-1}) is obviously more intense than that in the PtAl spectrum (2100 cm^{-1}) and a new band at 2162 cm^{-1} , assigned to CO linearly adsorbed on Pt^{2+} or Pt^{3+} , is observed which indicates that Pt on the $\text{CeO}_2\text{-ZrO}_2$ is more highly electron-deficient due to the alkaline nature of the support [14–17]. No obvious CO adsorption bands are seen in the spectrum of the CeZr sample.

3.3. Redox and OSC properties

The H_2 -TPR profiles shown in Fig. 4 describe the redox properties of the catalysts. The PtAl exhibits a peak at $395\text{ }^\circ\text{C}$ corresponding to the reduction of PtO_x which has interacted with Al_2O_3 [18]. The $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ mixed oxide (CeZr) shows an intense peak at $520\text{ }^\circ\text{C}$, which is ascribed to the reduction of bulk oxygen in the $\text{CeO}_2\text{-ZrO}_2$ solid solution [19]. The intense peak at $98\text{ }^\circ\text{C}$ obtained for PtCeZr results from the reduction of both PtO_x and superficial $\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2$ due to the strong interaction between Pt and the support. This interpretation is supported by the absence of the peak at $495\text{ }^\circ\text{C}$ for the CeZr sample [20] and is attributed to the ability of the supported precious

metal to activate H_2 and then to spill it over onto the support [21]. In the absence of the precious metal, H_2 activation is difficult and becomes the rate-determining step for the reduction reaction [19]. There is a weak H_2 consumption peak at ca. $270\text{ }^\circ\text{C}$ for the PtCeZr, which is assigned to the removal of oxygen from a small percentage of the unpromoted $\text{CeO}_2\text{-ZrO}_2$ powder.

The OSC data provide information concerning the utilization of various oxygen species on different catalysts, and it has been reported that H_2 consumption in H_2 -TPR has a close connection with the total OSC of a given material [22]. At $450\text{ }^\circ\text{C}$, the DOSC values of the catalysts were 306, 858, and $492\text{ }\mu\text{mol CO}_2/\text{g-cat.}$ for PtAl, PtCeZr, and CeZr, respectively. The DOSC sequence of $\text{PtCeZr} > \text{CeZr} > \text{PtAl}$ indicates that Pt species play an important role in accelerating the release of bulk oxygen in the CeO_2 -based oxides. This result is in good agreement with the work of Bedrane et al. [10] who demonstrated that the Pt component may act as a porthole by which the active oxygen both enters and leaves the $\text{CeO}_2\text{-ZrO}_2$ catalyst.

3.4. Catalytic activity for NO and soot oxidation

Since NO_2 is required to initiate and propagate soot oxidation under loose contact conditions, the oxidation of NO to NO_2 is an important step during catalytic soot oxidation in the presence of NO and O_2 [11,23]. Figure 5(a) shows the effluent NO_2 concentration during NO-TPO trials over different catalysts, from which it can be seen that PtAl and PtCeZr exhibit

Fig. 3. IR spectra of CO adsorbed on the catalyst samples.

Fig. 4. H_2 -TPR profiles of the catalyst samples.

Fig. 5. Evolution of NO_2 during NO-TPO (a) and soot-TPO trials (b) over PtAl (1), PtCeZr (2), and CeZr (3). Reactant gas: 1000 ppm NO/10% O_2/N_2 .

similar NO oxidation activity. The former generates a slightly larger amount of NO_2 below 300 °C, while the latter produces slightly more NO_2 in the range of 300–400 °C. Compared to the Pt-containing catalysts, CeZr exhibits rather low NO oxidation activity, demonstrating the important role of Pt species. Meanwhile, as shown in Fig. 5(b), almost no NO_2 is observed during the soot-TPO reaction over CeZr until the temperature reaches 500 °C, at which point the majority of soot has been oxidized, while small downstream NO_2 concentrations (~100 ppm) are observed during the soot-TPO process over PtAl and PtCeZr.

Figure 6(a) shows the TPO curves obtained during soot oxidation over different catalysts under either NO + O_2 or O_2 while the light-off temperature (T_{50}) data are summarized in Table 2. Under both atmospheres, these catalysts uniformly exhibit high CO_2 selectivity (> 98%). During the soot-TPO tests performed in 1000 ppm NO/10% O_2/N_2 , the T_{50} values of the catalysts follow the order of PtCeZr < PtAl $\approx$ CeZr, indicating an enhancement of the catalytic activity due to the promotion effect of Pt on CeZr. These results appear, to some extent, inconsistent with the NO-TPO results, in which the NO_2 productivity over the catalysts follows a different order of PtCeZr $\approx$ PtAl > CeZr. That is, the CeZr catalyst, while displaying lower NO oxidation activity, exhibits similar soot oxidation activity to that over the PtAl, while the NO oxidation activity over the PtCeZr and PtAl catalysts are similar even though PtCeZr obvi-

ously possesses higher soot oxidation activity. These results imply that, in addition to the important role of NO_2 as a strong oxidizing agent, other factors are also involved in the soot oxidation reaction over the $\text{CeO}_2\text{-ZrO}_2$ -based catalysts.

The active oxygen generated by the $\text{CeO}_2\text{-ZrO}_2$ mixed oxide and promoted by the precious metal significantly improves the soot oxidation and so the soot-TPO tests were performed in O_2 to exclude the influence of NO_x . As shown in Fig. 6(b) and Table 2, the T_{50} values over the catalysts in the absence of NO follow the order of PtCeZr < CeZr < PtAl, indicating the superior performance of the $\text{CeO}_2\text{-ZrO}_2$ -based catalysts with regard to PtAl should be ascribed to the active oxygen resulting from the mixed oxide [7,11].

It has been suggested, however, that the further oxidation of the SOC_s generated by the reaction of NO_2 and soot represents the rate determining step in the soot oxidation process

Table 2

T_{50} (°C) values obtained for catalysts during soot-TPO in different atmospheres.

Catalyst	$T_{50}/^\circ\text{C}$		
	1000 ppm NO/10% O_2/N_2		10% O_2/N_2
	Catalyst + soot	Catalyst + soot	Catalyst + Nsoot
PtAl	464	515	525
CeZr	460	510	506
PtCeZr	430	507	489
—	570	575	572

Fig. 6. Soot conversion over various catalysts during soot-TPO in 1000 ppm NO/10% O_2 (a) and soot/Nsoot-TPO in 10% O_2 (b).

[4,23,24]. As indicated in Ref. [24], the NO_2 -pretreated “Nsoot” contains a larger amount of surface oxygen complexes than Printex-U does, thus a comparison between Nsoot- and soot-TPO is sufficient to demonstrate the effectiveness of catalysts on the deep oxidation of soot. As shown in Fig. 6(b) and Table 2, PtAl exhibits reduced catalytic activity for Nsoot oxidation, with the T_{50} shifting towards higher temperatures by ca. 10 °C compared with the value obtained for soot oxidation. On the contrary, the pretreatment of soot under NO_x decreases the light-off temperature of CeZr and especially of PtCeZr, demonstrating the accelerated deep oxidation of soot over the CeO_2 -ZrO₂-based catalysts.

3.5. In situ DRIFT spectra

To confirm the accelerated dissociation of SOCs over the CeO_2 -ZrO₂-based catalysts, *in situ* FTIR experiments were per-

formed. The DRIFT spectra of adsorbed species on the soot-free catalyst and catalyst+soot mixtures under the reaction atmosphere (1000 ppm NO in 10% O_2/N_2) were recorded and the results are shown in Fig. 7. The results confirmed the formation of nitrites, nitrates, and some SOCs on the catalyst surface. A summary of the band assignments is presented in Table 3.

In the absence of soot, PtAl exhibits bands corresponding to chelating bidentate nitrates (1546 and 1329 cm^{-1}) and bridging bidentate nitrates (1619 and 1229 cm^{-1}) on Al_2O_3 , as shown in Fig. 7(a). All the bands increase in intensity as the temperature is raised from 100 to 250 °C. At higher temperatures, with the decomposition of nitrates, the bands drop sharply in intensity and disappear almost completely at 500 °C. The band at ca. 1407 cm^{-1} can be assigned to nitro compounds, which are unstable and transform rapidly to nitrate species with increasing temperature. Compared with PtAl, these bands remain relatively constant in intensity in the PtCeZr and CeZr spectra ac-

Fig. 7. DRIFT spectra of PtAl (a), PtAl + soot (b), PtCeZr (c), PtCeZr + soot (d), CeZr (e), and CeZr + soot (f) exposed to 1000 ppm NO 10% O_2/N_2 at different temperatures.

Table 3IR assignments for adsorbed NO_x species.

Band (cm ⁻¹)	NO _x species	Mode	Ref.
1640–1610	Bridging bidentate nitrate	$\nu(\text{N=O})$	[25,28–32]
1270–1210		$\nu_{\text{as}}(\text{NO}_2)$	
1590–1540	Chelating bidentate nitrate	$\nu(\text{N=O})$	[25,26,29,30,32]
1340–1280		$\nu_{\text{as}}(\text{NO}_2)$	
1325–1300	Bridging bidentate nitrite	$\nu_{\text{as}}(\text{NO}_2)$	[28–32]
1230–1205		$\nu_{\text{sym}}(\text{NO}_2)$	
1550, 1257	Monodentate nitrate	$\nu_{\text{as}}(\text{NO}_2)$	[29,32]
		$\nu_{\text{sym}}(\text{NO}_2)$	
1440–1325	Nitro compound	$\nu_{\text{as}}(\text{NO}_2)$	[28,31]
		$\nu_{\text{sym}}(\text{NO}_2)$	

quired at high temperatures (Figs. 7(c) and 7(e)) due to the basic nature of the CeO₂-ZrO₂ support.

As shown in Fig. 7(b), (d), and (f), due to the pronounced light absorbance of the soot, the catalyst+soot mixtures exhibit lower band intensity compared with the soot-free samples. After mixing with the soot, an extra band appears at 1768 cm⁻¹ in the spectra of the PtAl + soot mixture at 300 °C above. This band is generally attributed to anhydride, lactone, and carboxylic species formed on the surface of the soot, all of which are considered to be intermediate products of the partial oxidation of soot by NO_x and O₂ [23,24]. These species are not observed, however, in the IR spectra of the PtCeZr + soot mixture and do not appear in the case of the CeZr + soot mixture until the temperature reaches 450 °C. These results indicate that the CeO₂-ZrO₂-based catalysts either inhibit the formation of SOCs or accelerate their decomposition. Based on the Nsoot-TPO results, the latter case is more plausible. This acceleration effect of the CeO₂-ZrO₂ mixed oxides can be further promoted with the participation of Pt.

3.6. Discussion

Based on our understanding of the soot oxidation mechanism, the acceleration of the oxidation rate should involve the formation and decomposition of SOCs [4]. In the case of the Pt/Al₂O₃ catalyst without the participation of active oxygen from the support, the oxidation reaction will be dominated by NO₂-assisted soot combustion according to the following equations.

Here Eq. (1) expresses the dissociation of gaseous oxygen at the active Pt sites (Pt^{*}). Gaseous NO can then be oxidized by the resulting oxygen species (O^{*}) at the Pt surfaces (Eq. (2)) resulting in NO₂, a powerful oxidant which can then efficiently ignite the soot by attacking the soot surface and generating SOCs (Eq. (3)). These SOCs may, in turn, be further oxidized to yield CO₂, either by NO₂ (Eq. (4)) or by reactive oxygen species (Eq. (5)). The NO that is generated (Eqs. (3) and (4)) can be re-oxidized, (Eq. (2)), resulting in the recycling of NO_x. We can use “NO₂ efficiency” [24] to establish the efficiency of the NO ↔ NO₂ ↔

soot cycle over a specific catalyst. The calculated NO₂ efficiency values are 2.1 and 4.7 for PtAl and PtCeZr at 400 °C, at which temperature the NO oxidation rate was at its approximate maximum for all the catalysts and the O₂-assisted combustion of the soot was severely limited. It is therefore obvious that the PtCeZr catalyst is more effective than the Pt/Al₂O₃ in terms of NO₂ utilization during the soot oxidation reaction. This is likely associated with the utilization of active oxygen from the CeO₂-ZrO₂ support. In the presence of NO_x, the interaction of NO₂ with oxygen vacant Ce atoms results in the formation of active oxygen, possibly in the form of peroxide or superoxide [4,33], as in the following equations.

The back spillover of the active oxygen generated (Eq. (7)) onto the Pt active sites can enhance the NO oxidation (Eq. (2)) and thereby accelerate the subsequent catalytic reactions (Eqs. (3) and (4)), resulting in a high NO ↔ NO₂ recycling efficiency and more opportunity for the NO₂-soot reaction to generate SOCs.

The decomposition of the SOCs is considered to be the rate-determining step during catalytic soot oxidation by some researchers [4]. The oxidation rate of the SOCs becomes obvious only at temperatures higher than 400 °C [4,25], leading to the thermal decomposition of NO₂ into inactive NO, thus making the oxidation of SOCs more difficult in the absence of the powerful oxidant NO₂ [34,35]. As indicated by Makkee et al. [9], the role of CeO₂-based catalyst is to cause spillover of active oxygen onto the soot surface and its subsequent adsorption by the SOCs is an intermediate step in the soot oxidation mechanism, although only the first few reducible surface layers of the catalyst are important. Thus the soot oxidation activity is determined by the transfer capability of the active oxygen on the surface rather than the bulk OSC of the catalyst. It has been reported that the oxidation of CO on PtCeZr primarily takes place on the surface of the precious metal particles and follows an Eley-Rideal mechanism [19] as shown below.

Eq. (8) indicates the formation of CO₂ on the metal surface and Eq. (9) represents the subsequent desorption of this CO₂. Thus the formation and transfer of active oxygen species to the catalyst surface (Eqs. (6),(7)) are important steps in CO oxidation. In this study, the alternation of CO and O₂ pulses occurred at intervals of only 5 s and thus the DOSC of the catalyst was determined to a significant extent by the active oxygen transfer. Since chemisorbed oxygen species on the Pt have been reported to play an important role in the catalytic oxidation of the SOCs, a large amount of active oxygen must be rapidly transferred from the CeO₂-ZrO₂ and Pt surface to the SOCs, achieving a remarkably accelerated decomposition of the SOCs on the PtCeZr, as evidenced by the Nsoot-TPO and FTIR results [36]. Because the further oxidation of the SOCs is crucial to the soot oxidation process, the PtCeZr exhibits a low T₅₀ during soot combustion under both NO + O₂ and O₂. The T₅₀ values of all the catalysts during soot-TPO in the presence of NO_x as well as the T₁₀ values obtained from Nsoot-TPO under O₂ are all around

Fig. 8. Relationship between the DOSC values and soot oxidation activity of the catalysts in different atmospheres.

Fig. 9. Mechanisms of soot oxidation over Pt/Al₂O₃ and Pt/Ce_{0.6}Zr_{0.4}O₂ in the presence of NO + O₂.

450 °C, and these values are compared with the DOSC values obtained at 450 °C in Fig. 8. It is noteworthy that a higher DOSC always results in a lower soot/Nsoot oxidation temperature.

No active oxygen is provided by Al₂O₃ in the case of the PtAl catalyst and so, once the chemisorbed oxygen species on the Pt are consumed, they can only be restored by gaseous O₂ which has been absorbed and activated on the Pt. Thus, although this catalyst exhibits good NO oxidation activity, it shows poor NO₂ utilization and O₂-assisted soot oxidation activity. As for the CeZr catalyst, it has many more active oxygen species than PtAl, as indicated by the H₂-TPR result. However, the lack of Pt to act as a porthole leads to low utilization of these oxygen species, resulting in an elevated H₂ reduction temperature and a relatively low DOSC value at 450 °C for CeZr. Even so, the CeZr catalyst still exhibits some promotion effect during Nsoot oxidation, indicating that the active oxygen can accelerate the deep oxidation of soot even without the participation of Pt. Proposed schemes for the surface reaction processes over PtAl and PtCeZr are presented in Fig. 9.

4. Conclusions

Under loose contact conditions, a Pt catalyst supported on CeO₂-ZrO₂ exhibits similar catalytic activity for NO oxidation to that of an Al₂O₃-supported catalyst but also presents obviously higher activity for soot oxidation under NO+O₂, with a decrease of 34 °C of T₅₀. This increased activity is due to the high oxygen mobility in the mixed oxide and the synergistic effect between the precious metal and the support. Based on the high DOSC value of Pt/CeO₂-ZrO₂ catalyst, nearly twice that obtained with

PtAl, the active oxygen on Pt/CeO₂-ZrO₂ can be effectively utilized to improve the NO ↔ NO₂ ↔ soot recycling process. This results in ready oxidation of the SOCs that form during this recycling, leading to elevated soot oxidation activity under both O₂ and NO + O₂.

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Graphical Abstract

Chin. J. Catal., 2014, 35: 407–415 doi: 10.1016/S1872-2067(14)60004-8

Active oxygen-assisted NO-NO₂ recycling and decomposition of surface oxygenated species on diesel soot with Pt/Ce_{0.6}Zr_{0.4}O₂ catalyst

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The synergistic effect between Pt and CeZr increases the availability of active oxygen which in turn accelerates NO ↔ NO₂ recycling and the oxidation of SOCs, resulting in enhanced catalytic activity during soot oxidation.

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Pt/Ce_{0.6}Zr_{0.4}O₂催化剂催化氧化碳烟过程中活性氧对NO-NO₂循环及表面含氧物种的分解作用

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摘要: 通过在Ce_{0.6}Zr_{0.4}O₂载体上浸渍Pt(NO₃)₂制得Pt/Ce_{0.6}Zr_{0.4}O₂催化剂, 该催化剂在松散接触条件下, 于NO + O₂或O₂气氛中均表现出比Pt/Al₂O₃更好的碳烟氧化性能。进一步研究表明, Pt/Ce_{0.6}Zr_{0.4}O₂催化剂中的Pt与Ce_{0.6}Zr_{0.4}O₂存在相互作用, 使得催化剂在一定温度范围内对活性氧的利用率大为提高, 从而促进了气氛中NO ↔ NO₂的循环, 乃至碳烟与NO₂的反应和碳烟表面含氧中间物种的生成; 更重要的是, 这部分活性氧本身可加速含氧中间物种的分解。因此, 在NO + O₂的气氛中, Pt/Ce_{0.6}Zr_{0.4}O₂催化剂的碳烟起燃温度比Pt/Al₂O₃降低了34 °C。

关键词: 铂催化剂; 铈锆复合氧化物; 碳烟氧化; 一氧化氮-二氧化氮循环; 表面含氧物种

收稿日期: 2013-11-09. 接受日期: 2013-12-13. 出版日期: 2014-03-20.

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基金来源: 国家自然科学基金(51072096); 国家重点基础研究发展计划(973计划, 2010CB732304); 国家高技术研究发展计划(863计划, 2013AA065302).

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