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Article

Effect of Y on improving the thermal stability of $\text{MnO}_x\text{-CeO}_2$ catalysts for diesel soot oxidation

Hailong Zhang ^a, Jianli Wang ^a, Yi Cao ^a, Yijing Wang ^b, Maochu Gong ^a, Yaoqiang Chen ^{a,c,*}^a Key Laboratory of Green Chemistry and Technology of the Ministry of Education, College of Chemistry, Sichuan University, Chengdu 610064, Sichuan, China^b Ningbo Yuanxiang Energy Saving and Environmental Protection Technology Company, Ningbo 315800, Zhejiang, China^c Sichuan Provincial Environmental Catalytic Material Engineering Technology Center, Chengdu 610064, Sichuan, China

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ABSTRACT

A series of $\text{MnO}_x\text{-CeO}_2\text{-Y}_2\text{O}_3$ catalysts with different Y loadings (0, 1, 3, 6, and 10 wt%) were prepared by a co-precipitation method and investigated for NO_x -assisted soot oxidation. The thermal stabilities of these catalysts were evaluated by treating them at 800 °C for 12 h under dry air flow. The catalysts were characterized by X-ray diffraction, N_2 adsorption-desorption, Raman spectroscopy, H_2 temperature-programmed reduction, oxygen storage capacity, NO temperature-programmed oxidation, X-ray photoelectron spectroscopy, and soot temperature-programmed oxidation. The addition of Y led to decreased BET surface areas and poor low-temperature reduction abilities and oxygen storage capacities, which affected NO and soot oxidation activities. However, after aging, the doping of Y had effectively enhanced the stability of the catalytic activities for NO and soot oxidations, where the addition of 6%–10% Y achieved the optimum result because the maximal soot oxidation rate temperature was increased by only 34–35 °C. Additionally, the catalytic activity and deactivation of $\text{MnO}_x\text{-CeO}_2$ -containing catalysts were closely related to the presence of Mn^{4+} and oxygen species on the surface.

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1. Introduction

In recent years, diesel engines have been more and more widely used in heavy duty vehicles because of their high efficiency and low fuel consumption compared with petrol engines. However, the particulate matter (PM) emissions, which cause environmental pollution and adverse health effects, have become a drawback of diesel engines [1–3]. To reduce PM emissions and protect human health, emission standards and legislations of the acceptable levels have been defined in Europe, which demand an after-treatment of the exhaust gases.

The main composition of PM is carbonaceous particles (soot), in which $\text{PM}_{2.5}$ (particles of sizes below 2.5 μm) adsorb carcinogens, such as aromatic compounds, and can easily enter the human body by respiration and lead to serious health risks [4,5]. Diesel particulate filters (DPFs) for the elimination of soot PMs exhibit a high filtering efficiency (> 99%) [6]. However, under engine operating conditions, a low exhaust temperature (200–400 °C) cannot ignite the soot particles because of their high uncatalyzed oxidation temperature of around 600 °C. The most feasible route for soot combustion at low exhaust temperatures is a catalytic DPF technology combining filtration and

* Corresponding author. Tel/Fax: +86-28-85418451; E-mail: nic7501@scu.edu.cn

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catalytic oxidation of soot. Thus, soot oxidation catalysts such as noble metal catalysts [7–9], perovskite-type oxides [10], and ceria-based oxides [11–14] have been widely investigated.

Under conventional conditions, the contact between soot and catalyst in the catalyzed DPF is poor, which affects the catalytic activity for soot oxidation [15]. Generally, NO_2 contained in the exhaust gases can easily mix with and oxidize soot at low temperatures in the range of 250–400 °C because of its excellent molecular diffusion and stronger oxidizing ability than O_2 [16–18]. Therefore, the oxidation of soot by NO_2 does not depend on the mass transfer conditions nor require a high temperature, and NO_2 is considered an important and desirable oxidant under normal conditions. Although the amount of NO_x in diesel exhaust is low (100–700 ppm), using a catalyst can increase NO_2 concentration and promote soot combustion by which NO can be oxidized to NO_2 [19]. However, because more O_2 (5%–15%) is present than NO_2 in diesel exhaust gases, further study is needed to improve the availability of oxygen for use by catalysts during soot oxidation [20,21].

Oi-Uchisawa et al. [22] found that the supported noble metal Pt catalysts had remarkable promoting effects on the oxidation of soot due to their high catalytic activity of oxidizing NO to NO_2 . This Pt-containing catalyst may be ideal for soot oxidation under loose contact conditions. However, the high cost and scarcity of Pt have urged many researchers to study new catalysts for soot oxidation. $\text{MnO}_x\text{-CeO}_2$ mixed oxides are effective for soot catalytic oxidation in both O_2 - and NO_x -assisted conditions [23,24]. One important finding is that the introduction of Mn^{x+} into ceria improves the mobility of lattice oxygen and promotes catalytic activity because of the synergistic effects of $\text{MnO}_x\text{-CeO}_2$ mixed oxides [25,26]. In addition, the nitrate storage capacity of $\text{MnO}_x\text{-CeO}_2$ was reported at low temperature, and NO_2 was released into the gas phase to oxidize soot at high temperature [27]. The mixed oxides exhibited a high catalytic activity for NO oxidation to NO_2 , which was higher than those of the supported-Pt catalysts [23].

However, $\text{MnO}_x\text{-CeO}_2$ catalysts often show poor thermal stability under high-temperature conditions, which leads to severe catalyst deactivation and decreases the selectivity to CO_2 produced during the soot oxidation process [18,28]. Thus, the thermal stability of $\text{MnO}_x\text{-CeO}_2$ catalysts is considered an important aspect for further study. Y is an excellent promoter that can improve both the catalytic activity and thermal stability in many catalytic fields. In the study by He et al. [29], the addition of Y increased the concentration of oxygen vacancies and improved the mobility of oxygen. In the study by Wang et al. [30], a catalyst with 5% Y loading for C_3H_8 oxidation exhibited a high thermal stability even after thermal treatment at 1100 °C. Additionally, the incorporation of Y retains sulfur and water-vapor resistances [30,31].

In the present study, a series of Y^{3+} -modified $\text{MnO}_x\text{-CeO}_2$ catalysts with different Y loadings were prepared by a co-precipitation method. Aging treatments were performed at 800 °C for 12 h to investigate the thermal stabilities of the catalysts. To explore the possible effect of thermal aging on catalytic activity for soot oxidation, the catalysts were characterized by a series of structural and surface property measurements.

2. Experimental

2.1. Preparation of the catalysts

A series of $\text{MnO}_x\text{-CeO}_2\text{-Y}_2\text{O}_3$ mixed oxides with an Mn/Ce molar ratio of 1:4 and different Y dopings (0, 1, 3, 6, and 10 wt%) were prepared by co-precipitation. The precursors $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (95%), $\text{Mn}(\text{NO}_3)_2$ (50 wt%), and $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.5%) were dissolved in deionized water and then mixed with a buffer solution consisting of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{CO}_3$. The pH was controlled at 9.0. The precipitates obtained were filtered and dried at 90 °C for 12 h, then calcined in air at 500 °C for 3 h in a muffle furnace. These samples with different Y dopings of 0, 1, 3, 6, and 10 wt% were labeled as Cat. 1, Cat. 2, Cat. 3, Cat. 4, and Cat. 5, respectively. The aged catalysts were obtained by thermal treatment at 800 °C for 12 h and denoted with a prefix of “A-”.

2.2. Characterization of the catalysts

Powder X-ray diffraction (XRD) was performed on a D/max-RA diffractometer (Japan Science, Rigaku, Tokyo, Japan) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154056$ nm). The X-ray tube was operated at 40 kV and 40 mA. The XRD patterns of samples were recorded in the range of $20^\circ \leq 2\theta \leq 80^\circ$ with a scanning step size of 0.06° . The average crystalline size (D) of ceria (111) was calculated using the Scherrer equation. Raman spectra of the catalysts were obtained on a LabRAM HR Raman spectrometer (Horiba Jobin Yvon, Paris, France) with a diode-pumped YAG laser (532 nm) and an Nd:Yag detector. A total of 100 scans at a 73.6 mW laser output power were recorded. The specific surface areas of the samples were measured on an automatic surface analyzer (Quantachrome Quadrasorb SI Instrument, Boynton Beach, FL, USA) using BET method by N_2 adsorption-desorption at -196 °C. Prior to the measurements, the samples were degassed at 300 °C for 3 h under vacuum. The H_2 temperature-programmed reduction ($\text{H}_2\text{-TPR}$) was investigated using a 100 mg sample in each measurement. The samples were pretreated with N_2 at 400 °C for 40 min and then cooled to room temperature, and the flow of 5% H_2/N_2 (30 mL/min) was introduced into the system. The samples were heated from room temperature to 800 °C at a rate of 8 °C/min. The consumption signals of H_2 were monitored by a thermal conductivity detector.

The oxygen storage capacity (OSC) measurements were carried out in a flow reactor system in pulse mode. First, the samples (200 mg) were reduced by H_2 for 30 min at a certain temperature and then purged by pure He for 5 min. Next, at the same temperature, the O_2 pulse measurements were operated, with 5 s pulses and 60 s outgassing of He between two adjoining O_2 pulses, to obtain the OSC values. The consumption signals of O_2 were monitored by a thermal conductivity detector. The test temperature range was from 200 to 600 °C with intervals of 100 °C. The NO temperature-programmed oxidation (NO-TPO) tests were conducted in a fixed-bed reactor with the effluent gases monitored by a NO- NO_2 - NO_x analyzer (Model 42i-HL, Thermo Scientific, Waltham, MA, USA). The catalyst

(200 mg) was heated to 650 °C in a tubular quartz reactor at a heating rate of 5 °C/min. A gas mixture of 800 ppm NO_x/10% O₂/N₂ (500 mL/min) was fed. The concentration of NO₂ is defined as $[\text{NO}_2] = [\text{NO}_2]_{\text{outlet}} / ([\text{NO}]_{\text{outlet}} + [\text{NO}_2]_{\text{outlet}}) \times 100\%$, where NO and NO₂ are the main products from the outlet. The X-ray photoelectron spectroscopy (XPS) measurements were conducted on an AXIS Ultra DLD spectrometer (Kratos, Manchester, UK) using Al K α radiation as the excitation source (300 W). The binding energy of adventitious carbon (C 1s) at 284.6 eV was used to correct the charging effect of samples. Prior to the measurements, the sample was placed under vacuum for 4 h at room temperature.

2.3. Catalytic activity measurement

The soot-TPO tests were carried out in the same apparatus used in the NO-TPO tests. The inlet gas mixture was 800 ppm NO_x/10% O₂/N₂ (500 mL/min, GHSV = 30000 h⁻¹). Printex-U (Degussa) was used as a model soot. Soot and catalysts were mixed using a spatula in a mortar at a mass ratio of 1:10, the contact was defined as “loose contact” and 100 mg of the mixture was used for the measurement. The reactor temperature was ramped to 700 °C from room temperature at a heating rate of 10 °C/min. CO_x (CO and CO₂) emission from soot oxidation was detected by a CO_x analyzer (FGA-4100, Foshan Analytical Instrument Co., Ltd, Foshan, China). The temperature at which maximal soot oxidation rate reached (T_m) was used to evaluate the catalytic activities for soot oxidation. The selectivity to CO₂ (S_{CO_2}) during soot oxidation was calculated by the ratio of CO₂/(CO₂ + CO).

3. Results and discussion

3.1. Catalytic activity for soot oxidation

Table 1 shows the maximal soot oxidation rate temperature (T_m) and the selectivity to CO₂ (S_{CO_2}) of the fresh and aged catalysts with different loadings of Y. Among the fresh catalysts calcined at 500 °C for 3 h, the Y-free catalyst Cat. 1 showed the best soot oxidation activity, whereas the Y³⁺-modified catalysts displayed poorer activities because of their higher T_m values. This result implies that the addition of Y into MnO_x-CeO₂ mixed oxides is detrimental to the improvement of soot oxidation activity. After 1% Y was doped into MnO_x-CeO₂, the catalytic activity decreased because the T_m increased by 54 °C from that of Cat. 1. With increasing content of Y doping, Y³⁺-modified catalysts showed stable soot oxidation activities because there

was only a slight change in T_m values (498–511 °C) among them. This result can be explained by two aspects. First, the fractional replacement of MnO_x-CeO₂ mixed oxides leads to the loss of soot oxidation activity. Second, the incorporation of Y induces the formation of more oxygen vacancies and improves the mobility of oxygen [29]. The relatively consistent activity results of Y³⁺-modified catalysts (specifically Cat. 3 and Cat. 4), with increased Y loadings, illustrate the importance of the mobility of oxygen.

After thermal aging, the T_m of Cat. 1 increased up to 617 °C from 434 °C, implying severe catalyst deactivation and poor thermal stability. However, the Y³⁺-modified catalysts retained catalytic activity and showed a higher thermal stability because of the low increase of T_m ($\Delta T_m = 34\text{--}79$ °C). Cat. 4 and Cat. 5 showed relatively higher stabilities because their T_m values increased by only 34–35 °C. The thermal stabilities of Y³⁺-modified catalysts increased with the increase of Y loading. When the Y content increased to 6%, a ΔT_m similar to that of 10% loading was observed, which indicates that the thermal stability of the catalysts plateaus within a specific range of Y-doping content.

The selectivities to CO₂ (S_{CO_2}) of fresh and aged catalysts were evaluated during the soot-TPO tests, and the results obtained are listed in Table 1. All the fresh catalysts showed a high CO₂ selectivity. However, after thermal treatment at a high temperature, the Y-free catalyst Cat. 1 exhibited the lowest CO₂ selectivity (48%). The addition of Y to MnO_x-CeO₂ inhibited the effect of thermal aging and retained CO₂ selectivity. Cat. 4 and Cat. 5 showed almost no apparent change in the CO₂ selectivities compared with those of the fresh catalysts. This result illustrates that 6%–10% Y loadings effectively stabilize the CO₂ selectivity of MnO_x-CeO₂ catalysts for soot oxidation.

3.2. XRD, Raman, and N₂ adsorption results

The XRD patterns of the fresh and aged catalysts are shown in Fig. 1, and the calculated cell parameters are listed in Table 2. All the samples displayed diffraction peaks typical of the fluorite-like CeO₂ phase. Compared with the lattice constant of pure CeO₂ (0.5417–0.5418 nm) [32], those of the fresh catalysts were lower, which was because of the partial incorporation of Mn^{x+} and Y³⁺ with smaller ionic radii (Mn⁴⁺ 0.053 nm, Mn³⁺ 0.065 nm, Mn²⁺ 0.083 nm, and Y³⁺ 0.090 nm) than those of Ce^{x+} (Ce⁴⁺ 0.097 nm and Ce³⁺ 0.114 nm) [23,28]. The diffraction peaks of manganese oxides were not observed in Fig. 1(a), suggesting a high dispersion of MnO_x species over all the fresh samples. After aging at a high temperature, particle sintering and crystalline growth of all the catalysts occurred as shown by the sharp diffraction peaks in Fig. 1(b). By comparison, A-Cat. 1 (0% Y) and A-Cat. 2 (1% Y) showed the strongest diffraction peaks and the largest crystalline size (about 28 nm). With increasing content of Y, those changes were gradually reduced. A-Cat. 4 (6% Y) and A-Cat. 5 (10% Y) exhibited better results than the others because the diffraction intensities were lower and crystalline sizes smaller (12.6–13.9 nm). These results demonstrate that the incorporation of 6%–10% Y effectively stabilizes the structural property of MnO_x-CeO₂ catalysts during

Table 1
Soot oxidation activities of the catalysts.

Catalyst	Fresh		Aged		ΔT_m (°C)
	T_m (°C)	S_{CO_2} (%)	T_m (°C)	S_{CO_2} (%)	
Cat. 1	434	98	617	48	183
Cat. 2	498	99	577	87	79
Cat. 3	505	99	568	91	63
Cat. 4	503	99	537	98	34
Cat. 5	511	99	546	98	35

Fig. 1. XRD patterns of the fresh (a) and aged (b) catalysts with different Y loadings.

Table 2

Structural properties of the catalysts.

Catalyst	d^a (nm)		D^b (nm)		S_{BET} (m ² /g)	
	Fresh	Aged	Fresh	Aged	Fresh	Aged
Cat. 1	0.5398	0.5403	4.3	28.1	116	8
Cat. 2	0.5391	0.5401	5.0	28.2	76	12
Cat. 3	0.5391	0.5398	4.5	21.1	65	16
Cat. 4	0.5378	0.5383	4.4	13.9	53	22
Cat. 5	0.5362	0.5385	4.4	12.6	40	22

^a Lattice constant of ceria calculated by Bragg's law from XRD data.

^b Crystallite size of ceria calculated by Scherrer equation from XRD data.

high-temperature treatment.

The diffraction peaks of manganese oxides on the aged catalysts are not clearly shown in Fig. 1(b). However, the lattice constants of the aged catalysts were higher than those of the fresh ones as displayed in Table 2, which illustrates a phase separation of $\text{MnO}_x\text{-CeO}_2$ mixed oxides as reported in studies by Liu et al. [23] and Wu et al. [28]. To investigate the structural features in detail of the aged catalysts and confirm the existence of phase separation of $\text{MnO}_x\text{-CeO}_2$ mixed oxides, Raman spectroscopy was conducted because of its sensitivity to M–O bond arrangements. The results of the selected catalysts (Cat. 1, Cat. 4, A-Cat. 1, and A-Cat. 4) are shown in Fig. 2. The fresh catalysts Cat. 1 and Cat. 4 exhibited bands at 439 and 443 cm^{−1}, respectively, ascribed to the symmetric O–Ce–O stretching vibration (F_{2g} model) of the fluorite-type structure. The lower

Fig. 2. Raman spectra of Cat. 1 (0% Y), Cat. 4 (6% Y), A-Cat. 1 and A-Cat. 4 catalysts.

wavenumbers than that of ceria (around 463 cm^{−1}) indicated the formation of a solid solution phase of $\text{MnO}_x\text{-CeO}_2$ or $\text{MnO}_x\text{-Y}_2\text{O}_3\text{-CeO}_2$ [23,33]. Additionally, Cat. 4 shows a lower Raman intensity than that of Cat. 1, suggesting that the addition of Y promotes the dispersion of $\text{MnO}_x\text{-CeO}_2$ solid solution [30]. The bands at around 444 and 456 cm^{−1} of the aged catalysts, A-Cat. 1 and A-Cat. 4, respectively, shifted towards higher wavenumbers compared with those of the fresh ones. This result implies the separation of the solid solution phases after aging as previously described in a study by Liu et al. [23]. The band at around 645 cm^{−1} of Mn_3O_4 cannot be clearly observed in Fig. 2. These results agree with those obtained by XRD.

The specific surface areas (S_{BET}) of the fresh and aged catalysts are listed in Table 2. The S_{BET} of the unmodified catalyst Cat. 1 showed the highest value (116 m²/g) among all the fresh samples. The decreased S_{BET} (40–76 m²/g) of the Y³⁺-modified catalysts demonstrate that the incorporation of Y affects the morphology of $\text{MnO}_x\text{-CeO}_2$ mixed oxides. After aging at a high temperature, the S_{BET} of all the catalysts decreased. A-Cat. 1 (0% Y) showed the lowest S_{BET} (only 8 m²/g). The addition of Y inhibited the reduction of S_{BET} , and A-Cat. 4 (6% Y) and A-Cat. 5 (10% Y) showed the highest retained surface area (22 m²/g). These results reveal that the structural and morphological properties of the catalysts are affected by high-temperature aging, leading to particle sintering, crystalline growth, phase separation, and decreased surface areas. Those effects often induce decreases in catalytic activity. The sintering and phase separation of $\text{MnO}_x\text{-CeO}_2$ catalysts can easily remove the interaction between Ce and Mn species and decrease the availability of active species, and weaken the redox performance of the catalyst, which is unfavorable to the soot oxidation activity [23,28]. In addition, the decreased surface area also affects the catalytic activity for soot oxidation as reported in the literature [11,20,24,28]. As shown in Table 1, the unmodified catalyst (Cat. 1) exhibited a large increase in T_m from 434 to 617 °C because of poor structural and morphological properties after aging. However, the incorporation of Y enhances the stability of soot oxidation activity, which is shown in the results of Cat. 4 (6% Y) and Cat. 5 (10% Y).

3.3. H_2 -TPR results

The H_2 -TPR profiles of the fresh and aged catalysts are shown in Fig. 3. MnO_x - CeO_2 mixed oxides have reportedly five distinct reduction peaks which appear at around 210, 280, 365, 415, and 510 °C [34,35]. The peaks that involve the reduction of MnO_x ($MnO_2/Mn_2O_3 \rightarrow Mn_3O_4 \rightarrow MnO$) and Ce^{4+} to Ce^{3+} cannot be assigned to specified reduction species or steps because of the multifactorial effects of reduction processes such as the oxidation state and crystallinity. The formation of CeO_2 - MnO_x solid solutions can promote the reduction of Mn species or Ce species [25,26,36]. In this study, for the fresh samples, the overlapped reduction peaks from 200 to 500 °C were observed in the H_2 -TPR profiles. Wang et al. [37] reported that the MnO_x - CeO_2 catalyst has three overlapped reduction peaks, which might be ascribed to the reduction of the “isolated” Mn^{4+} ions, Mn species in solid solution, and Mn and Ce species incurring a synergistic effect. In Wu’s study [28], the first overlapped peaks (at around 210 and 280 °C) were ascribed to the successive reduction of Mn species in the solid solution. The peaks at 365 and 415 °C were the reduction of $MnO_2/Mn_2O_3 \rightarrow Mn_3O_4$ and $Mn_3O_4 \rightarrow MnO$, respectively. The high-temperature peaks (> 500 °C) may be related to the reduction of Ce species. Figure 3 shows that the Y^{3+} -modified catalysts (Cat. 2–5) showed similar reduction features as those of the MnO_x - CeO_2 mixed oxide (Cat. 1). For Cat. 1, the reduction peaks at low temperature exhibited much stronger intensities in comparison with the high-temperature reduction peaks, which could be attributed to the high dispersion of reducible species on the catalyst of a high surface area. However, the addition of Y weakened the intensity of the low-temperature peaks, which could be related to the decrease of surface area. In summary, the Y-doped catalysts show reduced catalytic activities in the soot-TPO tests.

The surface reduction of CeO_2 at low temperatures can be promoted by the high dispersion of Mn species and the strong interaction between MnO_x and CeO_2 facilitates the reduction

Fig. 3. H_2 -TPR profiles of the fresh and aged catalysts.

ability of the catalyst at low temperatures [28,34]. Therefore, the fresh catalysts showed better low-temperature reduction properties. However, after thermal aging at 800 °C for 12 h, the low-temperature reduction peaks almost disappeared, and the H_2 consumption in the total reduction process also decreased for A-Cat. 1, A-Cat. 2, and A-Cat. 3. Interestingly, the catalysts A-Cat. 4 and A-Cat. 5 showed similar reduction profiles as those of the fresh catalysts apart from slightly decreased peak areas. As seen in the XRD and N_2 adsorption results, Cat. 1, Cat. 2, and Cat. 3 experienced more sintering than those of Cat. 4 and Cat. 5 during thermal aging, leading to the growth of the crystalline oxides and decreases of the S_{BET} . In addition, the Raman results demonstrate that high-temperature aging induces a separation of MnO_x - CeO_2 solid solutions. These factors combine to result in a decrease of the low-temperature reduction property because of the weakened interaction between MnO_x and CeO_2 as well as the decreased dispersion of reducible species. The low-temperature reduction ability is critical to the soot oxidation activity of the catalyst [28]. Thus, Cat. 1, Cat. 2, and Cat. 3 exhibited poor thermal stabilities and low soot oxidation activities after aging. Although, A-Cat. 4 and A-Cat. 5 showed better low-temperature reduction performance because of their higher thermal stabilities and catalytic activities than those of the other catalysts. The results also confirm that the addition of 6%–10% Y can stabilize the low-temperature reduction property of MnO_x - CeO_2 catalysts after thermal treatment at a high temperature.

3.4. OSC results

The OSC is important for the application of Ce-based catalysts. The OSC values of the fresh and aged catalysts at different temperatures are shown in Fig. 4. The OSC values of all the catalysts increased with increasing testing temperature until 400 °C. This trend is similar to the result of the dynamic OSC measurements from a study by Fan et al. [38]. However, most of the OSC values of the fresh catalysts decreased at high testing tem-

Fig. 4. OSC values of the fresh (solid line) and aged (dotted line) catalysts obtained by the O_2 pulses at different temperatures.

peratures ($> 400\text{ }^{\circ}\text{C}$) because of thermodynamic and kinetic effects.

At $200\text{ }^{\circ}\text{C}$, the OSC of the fresh and aged catalysts showed low values (below $50\text{ }\mu\text{mol/g}$), which indicates a low availability of active oxygen species on the surface of the catalysts at $200\text{ }^{\circ}\text{C}$. This result agrees with the H_2 -TPR results. For the fresh catalysts, with the increase of the testing temperature, the OSC of all the catalysts exhibited higher values ($120\text{--}250\text{ }\mu\text{mol/g}$) than those at $200\text{ }^{\circ}\text{C}$, which illustrates that high temperature conditions ($> 200\text{ }^{\circ}\text{C}$) are favorable to improve the mobility and availability of oxygen in the catalysts. In the H_2 -TPR results, the main reduction reactions of the catalysts occurred in the range of $220\text{--}480\text{ }^{\circ}\text{C}$. An increase of the OSC of the catalysts was observed in the same temperature range. This result indicates a close relationship between the OSC and reduction property of the catalysts. Moreover, at low temperatures ($< 400\text{ }^{\circ}\text{C}$), as shown in Fig. 4, Cat. 1 showed the highest OSC values among all the fresh catalysts, whereas the Y^{3+} -modified catalysts (Cat. 2–5) exhibited decreased OSC values. These results are consistent with those of the soot-TPO tests. This experiment reveals that a high OSC at low temperature ($< 400\text{ }^{\circ}\text{C}$) can enhance the soot oxidation activity of the catalysts. However, no relationships between the OSC values and soot oxidation activities of the fresh catalysts at high testing temperatures ($> 400\text{ }^{\circ}\text{C}$) were found from the soot-TPO and OSC results. This finding further illustrates that the soot oxidation activity is determined by the low-temperature OSC of the catalyst.

After thermal aging at a high temperature, all the catalysts showed decreased OSC values in comparison with those of the fresh catalysts. In the XRD, Raman, and N_2 adsorption results, thermal aging affected the structural and morphological properties of $\text{MnO}_x\text{-CeO}_2$ -containing catalysts, which may also result in the decrease in the OSCs of the aged catalysts. Interestingly, at low testing temperatures ($< 400\text{ }^{\circ}\text{C}$), A-Cat. 4 and A-Cat. 5 showed similar OSC values and were the highest among all the aged samples. A-Cat. 1 displayed the lowest value. This result reveals that the addition of Y effectively stabilizes the OSC of the catalysts, and 6%–10% Y exhibits the ideal result of increasing thermal stability. These findings agree with the results of the soot-TPO. The improvement of thermal stability on the soot oxidation activity depends on the stable low-temperature ($< 400\text{ }^{\circ}\text{C}$) OSC of the catalysts.

3.5. NO-TPO results

In the presence of NO, the $\text{MnO}_x\text{-CeO}_2$ -containing catalysts exhibit an advantage in the catalytic activity of soot oxidation, which has been confirmed by Liu et al. [23] and Wu et al. [28]. NO_2 is more effective than O_2 in oxidizing soot, thus the production of NO_2 is critical to the catalytic oxidation of soot in the presence of NO. Figure 5 shows the concentration of NO_2 production during the NO-TPO measurements. Of the fresh catalysts (Fig. 5(a)), Cat. 1 displayed the highest activity for NO oxidation to NO_2 , and the largest amount of NO_2 produced. The concentration of NO_2 production gradually decreased with the increase of Y doping. This result may be because of the fractional replacement of $\text{MnO}_x\text{-CeO}_2$ mixed oxides by Y_2O_3 . How-

Fig. 5. NO-TPO curves of the fresh (a) and aged (b) catalysts (without soot). Catalyst: 200 mg; reaction gas: 800 ppm NO_x /10% O_2 / N_2 .

ever, as shown in the N_2 adsorption and H_2 -TPR results, the addition of Y leads to the decrease of surface area and affects low-temperature reduction abilities, which could affect the catalytic activity for NO oxidation into NO_2 . In addition, the change in NO oxidation activity may influence soot oxidation activity. Compared with the soot-TPO results, Cat. 1 showed a higher NO_2 concentration and an improved soot oxidation activity compared with those of the other catalysts. The Y^{3+} -modified catalysts exhibited lower NO oxidation activities, of which Cat. 5 was the lowest, and lower catalytic activities for soot oxidation. After aging at a high temperature, all the catalysts exhibited decreased NO_2 concentrations. In Fig. 5(b), A-Cat. 1 showed the lowest NO oxidation activity because of both the decreased NO_2 concentration and the shift of the NO_2 production window towards a higher temperature. A-Cat. 2 and A-Cat. 3 exhibited a decrease in NO oxidation activity compared with those of the fresh catalysts. However, A-Cat. 4 and A-Cat. 5 showed smaller changes in NO oxidation activity, revealing higher thermal stabilities than those of the other catalysts. These results correlate well with the XRD, N_2 adsorption, H_2 -TPR, and OSC tests. The incorporation of 6%–10% Y into an $\text{MnO}_x\text{-CeO}_2$ solid solution effectively stabilizes the structural property, the reduction ability, and the oxygen storage capacity, and retain NO oxidation activity after aging. Therefore, Cat. 4 and Cat. 5 showed more stable soot oxidation activities after aging than those of the other catalysts. Additionally, the total amount of NO_2 production for the aged catalysts did not agree with the results of soot oxidation activity experiment. This finding indicates that the amount of NO_2 production is not the

Fig. 6. XPS spectra of the Cat. 1 (0% Y), Cat. 4 (6% Y), A-Cat. 1, and A-Cat. 4 catalysts.

only factor that affects the catalytic activity for soot oxidation.

3.6. XPS results

To further study the deactivation of the catalysts for soot oxidation, XPS measurements of the fresh and aged catalysts (Cat. 1, Cat. 4, A-Cat. 1, and A-Cat. 4) were conducted. The XPS spectra of the fresh and aged catalysts are shown in Fig. 6, and the results are summarized in Table 3. The Ce 3d XPS spectra can be resolved into eight peaks according to the presence of different Ce species [39]. As shown in Fig. 6, the peaks that are labeled as u''' , u'' , and u correspond to Ce $3d_{3/2}$ and v''' , v'' , and v to Ce $3d_{5/2}$ of Ce⁴⁺. The additional two peaks marked as v' and u' were also observed because of the presence of Ce³⁺. For the fitted XPS spectra of Mn 2p, the peak in the range of 641.6–642.9 eV was assigned to Mn³⁺ ions, and that in the range of 643.0–644.5 eV to Mn⁴⁺ ions [40]. The peak at a lower binding energy of 640.9 eV was attributed to Mn²⁺ ions. For O 1s spectra, the peaks at the binding energies of 529.1–530.0 and 531.3–531.8 eV correspond to lattice oxygen (O²⁻) and surface-adsorbed oxygen (O₂²⁻ or O⁻), respectively, and the peak above 533.0 eV was ascribed to adsorbed molecular water [36].

The chemical compositions located on the surface of the catalysts were suggested to have an important role in the soot oxidation activity. The catalytic activities are directly related to their surface chemical properties. Thus, the soot oxidation activities and thermal deactivation of the catalysts are related to the changes in surface chemical components. Table 3 lists the relative content of the surface chemical components of the cat-

alysts. For a single species Ce-based catalyst, the surface Ce species is the main active component and has a crucial effect on the catalytic activity. Furthermore, the surface Ce content and the ratio of Ce⁴⁺/Ce³⁺ are the main factors of the catalytic property. However, in this study, for MnO_x-CeO₂-containing catalysts, the addition of Y increased the relative content of Ce species in the fresh catalysts, and thermal aging leads to a decrease of Ce content as shown for Cat. 4 in Table 3. These results do not correlate with the catalytic activity results for soot oxidation. This finding reveals that the soot oxidation activity does not only depend on the surface Ce species for MnO_x-CeO₂-containing catalysts. As shown in this study, the soot oxidation activity is closely related to the low-temperature reduction property of the catalysts, and this mainly involves the surface Mn species. Therefore, the presence of surface Mn species determines the soot oxidation activity. As shown in Table 3, the catalyst Cat. 1 showed a higher relative content of Mn⁴⁺ than that of Cat. 4, which exhibited the opposite result. In the soot-TPO tests, the addition of Y caused the decrease of soot oxidation activity, which may be because of the decreased surface content of Mn⁴⁺ in the catalyst. Moreover, from the XPS results of the aged catalyst, the same conclusion is confirmed. The thermal deactivation of Cat. 1 can be related to the large decrease of Mn⁴⁺ content. Cat. 4 showed that the addition of Y stabilizes its structural property, but not its surface chemical components after aging. The thermal aging led to an increase of surface Mn⁴⁺ content from 0.42% to 1.80% for Cat. 4, which provides sufficient surface active species, and thus retained a higher reduction ability and OSC than those of Cat. 1, which is favorable to the catalytic oxidation of NO and soot.

Table 3

XPS results of the selected catalysts.

Catalyst	Element (at%)		Ce (at%)		Mn (at%)			O (at%)	
	Ce	Mn	Ce ⁴⁺	Ce ³⁺	Mn ⁴⁺	Mn ³⁺	Mn ²⁺	O _{latt}	O _{sur} + O _{ads}
Cat. 1	16.3	2.7	14.2	2.1	1.15	0.27	0.50	32.3	48.7
Cat. 4	21.3	2.8	18.4	2.9	0.42	0.89	0.52	43.9	32.0
A-Cat. 1	20.0	4.1	17.6	2.4	0.39	1.75	0.70	41.2	34.7
A-Cat. 4	8.3	4.1	7.2	1.1	1.80	0.61	0.30	26.5	62.1

In the H₂-TPR and OSC results, the soot oxidation activity was associated with both the reduction ability and the OSC at a low temperature. The two properties are related to the surface Mn species and the surface oxygen species. As shown in Table 3, Cat. 1 with a stronger reduction ability and higher OSC value of O_{sur} + O_{ads} than those of Cat. 4, which may be related to the high number of Mn⁴⁺ ions on the surface of Cat. 1 and promote soot oxidation activity. However, the O_{sur} + O_{ads} of Cat. 1 decreased after aging, which led to the deactivation of the catalyst during soot oxidation. Moreover, Cat. 4 showed an increased O_{sur} + O_{ads} value after aging, which inhibited catalyst deactivation. In addition, the oxidation activity of NO into NO₂ was influenced by the surface Mn and O species on the catalysts, affecting soot oxidation activity.

4. Conclusions

An MnO_x-CeO₂ catalyst was modified by introducing different loadings of Y₂O₃ oxide, and the effects of thermal stability on their soot oxidation activities were studied before and after aging treatment at 800 °C for 12 h. The soot-TPO results show that the addition of 6%–10% Y effectively retains NO_x-assisted soot oxidation activity because the T_m for soot oxidation increases by only 34–35 °C after aging. The superior thermal stability attributed to the introduction of Y can effectively inhibit the sintering of MnO_x-CeO₂ mixed oxides and retain a higher low-temperature reductions ability and OSC than those of the unmodified catalyst. Moreover, the NO-TPO results confirm a favorable thermal stability of NO oxidation activity for the catalysts with a doping of 6%–10% Y, which is beneficial for soot catalytic oxidation in the presence of NO. From the XPS results, a high surface content of Mn⁴⁺ and active oxygen species enhance the catalytic activity and inhibit the deactivation of the aged catalysts. Although the addition of Y cannot visibly promote soot oxidation activity of fresh catalysts, it can effectively improve their thermal stability. Therefore, the Y³⁺-modified MnO_x-CeO₂ catalysts are an ideal candidate to provide opportunities for applications to diesel exhaust filters.

References

- [1] Imran A, Varman M, Masjuki H H, Kalam M A. *Renew Sustain Energy Rev*, 2013, 26: 739
- [2] Wierzbicka A, Nilsson P T, Rissler J, Sallsten G, Xu Y Y, Pagels J H, Albin M, Österberg K, Strandberg B, Eriksson A, Bohgard M, Bergemalm-Rynell K, Gudmundsson A. *Atmos Environ*, 2014, 86: 212
- [3] Harrison P G, Ball I K, Daniell W, Lukinskas P, Céspedes M, Miró E, Ulla M A. *Chem Eng J*, 2003, 95: 47
- [4] Pui D Y H, Chen S C, Zuo Z L. *Particuology*, 2014, 13: 1
- [5] Chhiti Y, Peyrot M, Salvador S. *J Energy Chem*, 2013, 22: 701
- [6] Fino D, Specchia V. *Powder Technol*, 2008, 180: 64
- [7] Liu S, Wu X D, Weng D, Li M, Fan J. *Appl Catal B*, 2013, 138-139: 199
- [8] Matarrese R, Castoldi L, Artioli N, Finocchio E, Busca G, Lietti L. *Appl Catal B*, 2014, 144: 783
- [9] Liu S, Wu X D, Lin Y, Li M, Weng D. *Chin J Catal* (刘爽, 吴晓东, 林雨, 李敏, 翁端. 催化学报), 2014, 35: 407
- [10] Li Z Q, Meng M, Dai F F, Hu T D, Xie Y N, Zhang J. *Fuel*, 2012, 93: 606
- [11] Aneggi E, de Leitenburg C, Llorca J, Trovarelli A. *Catal Today*, 2012, 197: 119
- [12] Hernández-Giménez A M, Xavier L P S, Bueno-López A. *Appl Catal A*, 2013, 462-463: 100
- [13] Zhang G Z, Zhao Z, Xu J F, Zheng J X, Liu J, Jiang G Y, Duan A T, He H. *Appl Catal B*, 2011, 107: 302
- [14] Sheng Y Q, Zhou Y, Lu H F, Zhang Z K, Chen Y F. *Chin J Catal* (盛叶琴, 周瑛, 卢晗锋, 张泽凯, 陈银飞. 催化学报), 2013, 34: 567
- [15] Zouaoui N, Issa M, Kehrli D, Jeguirim M. *Catal Today*, 2012, 189: 65
- [16] Jeguirim M, Tschamber V, Brilhac J F. *J Chem Technol Biotechnol*, 2009, 84: 770
- [17] Jeguirim M, Villani K, Brilhac J F, Martens J A. *Appl Catal B*, 2010, 96: 34
- [18] Lin F, Wu X D, Liu S, Weng D, Huang Y Y. *Chem Eng J*, 2013, 226: 105
- [19] Azambre B, Collura S, Darcy P, Trichard J M, Da Costa P, García-García A, Bueno-López A. *Fuel Process Technol*, 2011, 92: 363
- [20] Muroyama H, Hano S, Matsui T, Eguchi K. *Catal Today*, 2010, 153: 133
- [21] Bueno-López A, Krishna K, van der Linden B, Mul G, Moulijn J A,

Graphical Abstract

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Effect of Y on improving the thermal stability of MnO_x-CeO₂ catalysts for diesel soot oxidation

Hailong Zhang, Jianli Wang, Yi Cao, Yijing Wang, Maochu Gong, Yaoqiang Chen*
Sichuan University;
Ningbo Yuanxiang Energy Saving and Environmental Protection Technology Company;
Sichuan Provincial Environmental Catalytic Material Engineering Technology Center

Addition of Y to MnO_x-CeO₂ improves thermal stability of the catalytic activity for soot oxidation, and 6%–10% Y exhibits the optimal best result. The activity and thermal deactivation of the catalysts are closely related to the presence of Mn⁴⁺ species.

- Makkee M. *Catal Today*, 2007, 121: 237
- [22] Oi-Uchisawa J, Wang S D, Nanba T, Ohi A, Obuchi A. *Appl Catal B*, 2003, 44: 207
- [23] Liu S, Wu X D, Weng D, Li M, Lee H R. *Chem Eng J*, 2012, 203: 25
- [24] Wu X D, Liu S, Weng D, Lin F. *Catal Commun*, 2011, 12: 345
- [25] Wu M, Wang X Y, Dai Q G, Gu Y X, Li D. *Catal Today*, 2010, 158: 336
- [26] Liu G, Yue R L, Jia Y, Ni Y, Yang J, Liu H D, Wang Z, Wu X F, Chen Y F. *Particuology*, 2013, 11: 454
- [27] Tikhomirov K, Kröcher O, Elsener M, Wokaun A. *Appl Catal B*, 2006, 64: 72
- [28] Wu X D, Liu S, Weng D, Lin F, Ran R. *J Hazard Mater*, 2011, 187: 283
- [29] He H, Dai H X, Ng L H, Wong K W, Au C T. *J Catal*, 2002, 206: 1
- [30] Wang G, You R, Meng M. *Fuel*, 2013, 103: 799
- [31] Wang G, Meng M, Zha Y Q, Ding T. *Fuel*, 2010, 89: 2244
- [32] Wu X D, Lin F, Xu H B, Weng D. *Appl Catal B*, 2010, 96: 101
- [33] Sato T, Komanoya T. *Catal Commun*, 2009, 10: 1095
- [34] Delimaris D, Ioannides T. *Appl Catal B*, 2008, 84: 303
- [35] Wu X D, Liu S, Lin F, Weng D. *J Hazard Mater*, 2010, 181: 722
- [36] Dai Y, Wang X Y, Dai Q G, Li D. *Appl Catal B*, 2012, 111–112: 141
- [37] Wang X Y, Ran L, Dai Y, Lu Y J, Dai Q G. *J Colloid Interface Sci*, 2014, 426: 324
- [38] Fan J, Wu X D, Liang Q, Ran R, Weng D. *Appl Catal B*, 2008, 81: 38
- [39] Wu X D, Xu L H, Weng D. *Appl Surf Sci*, 2004, 221: 375
- [40] Dai Y, Wang X Y, Li D, Dai Q G. *J Hazard Mater*, 2011, 188: 132

Y对柴油车碳烟氧化催化剂 $\text{MnO}_x\text{-CeO}_2$ 热稳定性的影响

张海龙^a, 王健礼^a, 曹毅^a, 王益静^b, 龚茂初^a, 陈耀强^{a,c,*}

^a四川大学化学学院, 绿色化学与技术教育部重点实验室, 四川成都610064

^b宁波远翔节能环保技术有限公司, 浙江宁波315800

^c四川省环境催化材料工程技术中心, 四川成都610064

摘要: 采用共沉淀法制备了不同Y含量的 $\text{MnO}_x\text{-CeO}_2\text{-Y}_2\text{O}_3$ 催化剂, 并用于 NO_x 存在条件下的碳烟氧化反应. 通过在干空气气流中800 °C焙烧12 h评价了这些催化剂的热稳定性. 采用X射线衍射、 N_2 吸附-脱附、拉曼光谱、 H_2 程序升温还原、储氧量测试、 NO 程序升温氧化、X射线光电子能谱和碳烟程序升温氧化等手段对催化剂进行了表征. 实验发现, Y的添加导致催化剂比表面积、还原性能和储氧能力下降, 从而影响了 NO 和碳烟的氧化活性. 然而, 热老化之后, Y可增大催化剂的热稳定性, 其中以6%–10% Y的添加效果最好, 它们的最大碳烟氧化速率温度仅增加了34–35 °C. $\text{MnO}_x\text{-CeO}_2$ 催化剂的催化活性和热失活与其表面的 Mn^{4+} 和氧物种密切相关.

关键词: $\text{MnO}_x\text{-CeO}_2\text{-Y}_2\text{O}_3$; 碳烟氧化活性; 热稳定性; 氧化还原性质; 氧储存能力

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*通讯联系人. 电话/传真: (028)85418451; 电子信箱: nic7501@scu.edu.cn

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