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# Highly active $\text{MnO}_x\text{-CeO}_2$ catalyst for diesel soot combustion†

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A series of  $\text{MnO}_x\text{-CeO}_2$  composites have been prepared via a facile coprecipitation method and used as catalysts for diesel soot combustion. It is found that the content of manganese oxide has a considerable influence on both the morphology and catalytic activity for diesel soot combustion in the copresence of  $\text{NO}_x$  and  $\text{O}_2$ . Superior catalytic activity ( $T_f = 360\text{ }^\circ\text{C}$ ) was obtained over the optimized catalyst  $\text{CM}_{20}$  [ $\text{Mn}/(\text{Mn} + \text{Ce})$  equals to 20 at%], which is believed to be attributable to the following two aspects: (1) the abundant pore structure, presenting between the loosely-packed homogeneous particles with similar sizes to that of the soot particles, which is beneficial for mass transfer and heat diffusion as well as the sufficient contact between catalyst and soot; (2) high concentration of  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations derived from the charge transfer between Mn and Ce species as active sites can adsorb and activate NO and  $\text{O}_2$ , and then greatly facilitate  $\text{NO}_2$  production.

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## 1. Introduction

Soot, as one of the main pollutants from diesel emission, has caused severe environmental problems like haze,<sup>1</sup> and several emission control strategies have been adopted to meet the demands of more and more stringent legislation, such as improvements in fuel oil,<sup>2</sup> modifications of the engine or process<sup>3,4</sup> and exhaust after-treatment systems.<sup>5</sup> For example, the diesel particulate filter (DPF) used in the after-treatment systems has so far been the most promising technological option. When the diesel exhaust flows through DPF, over 90% of the soot can be trapped and then be continuously or periodically combusted to  $\text{CO}_2$ .<sup>6</sup> However, the combustion temperature of soot (around  $600\text{ }^\circ\text{C}$ )<sup>7</sup> is far beyond the normal diesel exhaust temperature range ( $175\text{--}400\text{ }^\circ\text{C}$ ),<sup>8</sup> making the regeneration of DPF an intractable problem. Aimed at the passive regeneration of DPF, many kinds of catalysts, such as noble metals,<sup>9</sup> transition metal oxides,<sup>10</sup> perovskite and/or perovskite-like mixed oxides,<sup>11</sup> spinel mixed oxides,<sup>12</sup> alkaline metal/alkaline-earth metal oxides,<sup>13</sup> and the popular ceria-based oxides,<sup>14–19</sup> have

been developed to decrease the soot combustion temperature. Additionally, many researches demonstrate that the introduction of macropores or large voids into the catalysts can greatly facilitate the heat and mass transfer as well as improve the contact between soot and the catalysts, eventually to reach a high activity towards soot oxidation.<sup>11,20–25</sup> For example, Wei *et al.*<sup>23</sup> synthesized a three-dimensionally ordered macroporous (3DOM)  $\text{LaFeO}_3$  catalyst loaded with tiny golden nanoparticles ( $\sim 2.9\text{ nm}$ ), showing the temperature of maximum soot combustion rate ( $T_m$ ) at  $366\text{ }^\circ\text{C}$  under loose contact mode between soot and catalyst. Recently, Nascimento *et al.*<sup>25</sup> synthesized  $\text{Ag/CeO}_x/\text{FeO}_y$  catalysts supported on cordierite for the control of diesel soot emission, showing further decreased  $T_m$  ( $334\text{ }^\circ\text{C}$ ), and  $T_f$  (finishing soot combustion temperature,  $400\text{ }^\circ\text{C}$ ), exhibiting great potential in application. However, the high-cost, the sensitivity to sulfur, and easily sintering characteristic of noble metal catalysts,<sup>26,27</sup> as well as the difficulty in the synthesis of 3DOM materials hinder the industrial application of this kind of catalysts.

$\text{MnO}_x\text{-CeO}_2$  composites have been widely used in many catalytic reaction processes, such as wet oxidation of toxic organic pollutants<sup>28</sup> and oxidation of gaseous<sup>29</sup> or even liquid pollutants,<sup>30</sup> and proved to be a promising substitute for noble metal catalysts. But for catalytic soot combustion, the previously reported approaches are still hard to achieve a satisfactory performance on  $\text{MnO}_x\text{-CeO}_2$  composites, *i.e.*,  $T_m = 393\text{--}420\text{ }^\circ\text{C}$ ,  $T_f > 400\text{ }^\circ\text{C}$ , maybe due to the insufficient catalyst–soot contact that will restrict the full use of the active sites of the catalysts.<sup>10,31–34</sup>

Herein, a series of  $\text{MnO}_x\text{-CeO}_2$  composites was synthesized through a facile modified coprecipitation method. Especially,

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† Electronic supplementary information (ESI) available: Catalytic performance of samples reported in literatures together with  $\text{CM}_{20}$ , and NULL as reference; SEM images of  $\text{MnO}_x$ ,  $\text{CM}_y$  ( $y = 66, 50$  and  $5$ ),  $\text{CeO}_2$  and soot;  $\text{N}_2$  adsorption/desorption isotherms & pore size distributions of  $\text{CM}_{20}$  and  $\text{CM}_{33}$ ; structural properties and  $\text{H}_2$ -TPR profiles of all the catalysts studied, SEM-EDS results of different areas in  $\text{CM}_{33}$ . See DOI: 10.1039/c6ra25738k



the optimized catalyst CM<sub>20</sub> [Mn/(Mn + Ce) = 20 at%] shows uniform particle morphology with hierarchically porous structure which is much beneficial to the sufficient contact between catalyst and soot, as well as the high concentration of Mn<sup>4+</sup>–Ce<sup>3+</sup> cations on the surface that favors NO<sub>2</sub> production, thus exhibiting an excellent catalytic activity for the removal of soot in NO<sub>x</sub>/O<sub>2</sub> atmosphere, *i.e.*, ignition temperature ( $T_i$ ) = 280 °C,  $T_m$  = 326 °C and  $T_f$  = 360 °C. The possible catalytic mechanism for the soot combustion is also proposed.

## 2. Experimental

### 2.1 Catalyst preparation

All the chemicals used in this study were of analytical grade, and were used without further purification. MnO<sub>x</sub>–CeO<sub>2</sub> composites were prepared by the co-precipitation method reported before<sup>35</sup> with some modification. A typical preparation procedure is as follows: firstly, 7.5 mmol nitrate including Ce(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O and Mn(NO<sub>3</sub>)<sub>2</sub> (50 wt% in aqueous solution) was dissolved in 30 mL deionized water. Then, 30 mL water solution including 30 mmol NaHCO<sub>3</sub> was quickly poured into the nitrate solution and the mixture was stirred for 30 min at room temperature. Next, the precipitates were filtered and washed with deionized water and ethyl alcohol alternately for several times. After drying at 100 °C, the precursors were grinded and then calcined under static air at 500 °C for 2 h with a heating rate of 1 °C min<sup>-1</sup>. The obtained catalysts were designated CM<sub>y</sub>, where *y* (%) is the Mn/(Mn + Ce) atomic ratio in the recipe. In addition, we prepared two single oxides (CeO<sub>2</sub> and MnO<sub>x</sub>) for reference with the same synthesis condition.

### 2.2 Catalyst characterization

The nitrogen adsorption and desorption curves were obtained using Micromeritics Tristar 3000 at 77 K, and the specific surface area and the pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. Powder X-ray diffraction (XRD) patterns of the prepared samples were got using a Rigaku D/Max 2200 PC diffractometer with Cu K $\alpha$  radiation (40 kV and 40 mA). Field emission scanning electron microscopy (FE-SEM) imaging was performed using Hitachi S-4800. Transmission electron microscopy (TEM) images, selected area electron diffraction (SAED) patterns and element mapping images were obtained using a JEOL-2010F electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) signals were recorded using an ESCALab 250 instrument. The fitting of the Mn element was carried out using Gaussian fitting parameters. The temperature-programmed reduction with hydrogen (H<sub>2</sub>-TPR) experiments were performed using a Micromeritics Chemisorb 2750 instrument in a 5% H<sub>2</sub>/N<sub>2</sub> flow (25 mL min<sup>-1</sup>) using 50 mg catalyst with a heating rate of 10 °C min<sup>-1</sup>. The uptake amount of H<sub>2</sub> was measured using a thermal conductivity detector (TCD).

### 2.3 Activity testing

Carbon black from Degussa (diameters: 10–50 nm) was used as the model soot particles. Following a well-accepted procedure,

soot (10 mg) and catalyst (100 mg) were carefully mixed for 20 min with a spatula to simulate the loose contact mode, then silica pellets (1 g) were added and mixed by the spatula for another 10 min. It is worth noting that silica pellets were added to avoid pressure drop and favor heat transfer.<sup>36</sup> A gas mixture of 500 ppm NO, 10% O<sub>2</sub> and balance N<sub>2</sub> was feed with a flow rate of 200 mL min<sup>-1</sup>. The space velocity was thus calculated to be 120 000 mL (g h)<sup>-1</sup>. Afterwards, the mixture was heated to 650 °C at a heating rate of 5 °C min<sup>-1</sup> in a tube furnace equipped with a thermal couple. To minish the error of the measurement to a least extent, the temperature of the tube furnace was monitored with a standard thermal couple, every gas flow was verified with a mechanical flow meter and the concentration of NO<sub>x</sub> was measured by a NO<sub>x</sub> analyzer (Thermo Fisher 42i-LS). The analysis of the emissions from the reactor was performed using an online GC-FID analyzer (GC2060 from Shanghai Ruimin Instrument Corp. Ltd.) equipped with a methane converter. The catalytic activities (conversion and selectivity) were calculated as indicated in previous reports in the literature, in terms of  $T_i$ ,  $T_m$  and  $T_f$  values, which were respectively defined as the temperatures at 10%, 50% and 90% of soot conversion, and selectivity to CO<sub>2</sub> as well, which was quantified: selectivity (%) =  $S_{CO_2}(\text{total})/[S_{CO}(\text{total}) + S_{CO_2}(\text{total})]$ , where  $S_{CO_x}(\text{total})$  represents the area under the CO<sub>x</sub>-temperature curve in the range of RT – 650 °C ( $x = 1$  or 2).<sup>37,38</sup>

## 3. Results and discussion

### 3.1 Catalytic activity measurements

Fig. 1 shows the catalytic activity of the CM<sub>y</sub> composites, references MnO<sub>x</sub> and CeO<sub>2</sub>, and NULL (without catalyst) towards soot oxidation under loose contact mode. It is obvious that compared with NULL, all the CM<sub>y</sub> composites and the references MnO<sub>x</sub>, CeO<sub>2</sub> show much lower characteristic temperatures and higher selectivity to CO<sub>2</sub> in the soot oxidation. Thereinto, CM<sub>20</sub> shows the lowest characteristic temperatures ( $T_i$  = 280 °C,  $T_m$  = 326 °C, and  $T_f$  = 360 °C) as well as the highest selectivity to CO<sub>2</sub> (95.6%), indicating that the interaction between Mn and Ce species can greatly improve the catalytic activity toward the soot oxidation. Even compared with the noble-metal based catalysts supported on 3DOM oxides or

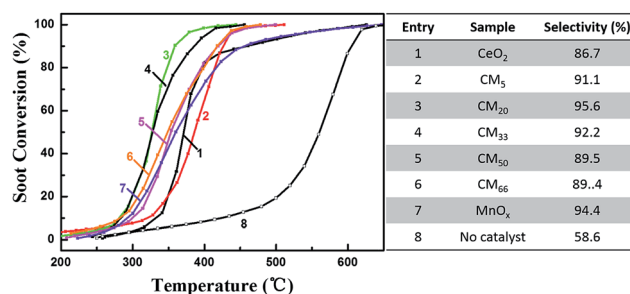


Fig. 1 Catalytic activity (left) and selectivity to CO<sub>2</sub> (right) for soot combustion over different catalysts or NULL (without catalyst) under loose contact mode. Reaction conditions: 500 ppm NO and 10% O<sub>2</sub> in N<sub>2</sub> with a total flow of 200 mL min<sup>-1</sup>, mass of soot–catalyst–silica is 10–100–1000 mg.



cordierite, as well as the  $\text{MnO}_x\text{-CeO}_2$  catalysts prepared by other methods,  $\text{CM}_{20}$  still shows much lower characteristic temperatures (especially  $T_i$ ) for soot combustion under similar reaction conditions (loose contact mode, shown in Table S1†). It should be noted that even at a higher space velocity [ $330\,000\text{ mL (g}_{\text{catal}}\text{ h)}^{-1}$ , the highest one among those shown in Table S1†],  $\text{CM}_{20}$  still shows a much lower  $T_m$  value ( $350\text{ }^\circ\text{C}$ ) than that of other reported  $\text{MnO}_x\text{-CeO}_2$  catalysts ( $393\text{--}420\text{ }^\circ\text{C}$ ) shown in Table S1.† Fig. S1 and S2† indicates good stability in both catalytic activity and structure for these  $\text{CM}_y$  composite catalysts (herein,  $\text{CM}_{33}$  was chosen as an example). In order to understand the different catalytic performances on these prepared catalysts, XRD analysis,  $\text{N}_2$  adsorption/desorption analysis and SEM/TEM observations were conducted to reveal both the phase composition and the morphology/pore structure of different catalysts.

### 3.2 XRD analyses

Fig. 2 shows the XRD patterns of different  $\text{CM}_y$  composites and the references  $\text{MnO}_x$  and  $\text{CeO}_2$ . It is found that the reference  $\text{CeO}_2$  exhibits a single phase of cubic  $\text{CeO}_2$  (JCPDS 43-1002), while  $\text{MnO}_x$  shows three distinguishable manganese oxides of  $\text{Mn}_2\text{O}_3$  (JCPDS 73-1826),  $\text{MnO}_2$  (JCPDS 72-1982) and  $\text{Mn}_5\text{O}_8$  (JCPDS 39-1218). In addition, compared with reference  $\text{CeO}_2$ , all the  $\text{CM}_y$  composites show relatively wide diffraction peaks corresponding to cubic  $\text{CeO}_2$  phase, without detectable Mn-containing phases or obvious peak shift, indicating that manganese oxides may exist in the form of highly dispersive and/or amorphous species, thus decreasing the crystallinity of  $\text{CeO}_2$ . More interestingly,  $\text{CM}_{20}$  shows the biggest FWHM (the full width at half maximum) values of the main XRD peaks among all the  $\text{CM}_y$  composites, suggestive of the smallest crystalline grain according to the Scherrer equation, and the corresponding most abundant surface defect sites, which are beneficial for the improvement of catalytic activity.

### 3.3 SEM & TEM measurements for $\text{CM}_{20}$

The typical SEM images and the corresponding EDS spectrum, as well as TEM image and the corresponding element mapping

of  $\text{CM}_{20}$  shown in Fig. 3 indicate that  $\text{CM}_{20}$  is solely composed of uniform particles with loose packing, leaving abundant large pores, as indicated by the arrows in Fig. 3b, which is very different from the morphologies of all the other studied catalysts in Fig. S3† ( $\text{CeO}_2$ ,  $\text{CM}_5$ ,  $\text{CM}_{50}$ ,  $\text{CM}_{66}$  and  $\text{MnO}_x$ ). The pore sizes in  $\text{CM}_{20}$  are measured to be within 16–103 nm (Fig. 3b), which are consistent with its pore size distribution (10–159 nm) by  $\text{N}_2$  adsorption/desorption analysis shown in Fig. S4† and summarized in Table S2.† As can be seen in Table S2,† the specific surface areas of  $\text{CM}_y$  composites are all larger than that of reference  $\text{MnO}_x$  and  $\text{CeO}_2$ . Especially,  $\text{CM}_{20}$  shows much enlarged specific surface area and pore volume as well. Besides, its pore size is also broadened. It is believed that the similar particle size of the sample  $\text{CM}_{20}$  to that of soot particles (Fig. S3–f†), and the abundant large pores in  $\text{CM}_{20}$  are both helpful to its sufficient contact with soot. Also, its high specific surface area and pore volume both favor the dispersion of active sites, thus making a great contribution to catalytic oxidation of soot. The atomic ratio of  $\text{Mn}/(\text{Mn} + \text{Ce})$  is calculated to be 21.9%, according to EDS spectrum in Fig. 3c, similar to that of the starting solution. As can be found in Fig. 3d–f, both the Ce species and Mn species are homogeneously distributed in the prepared composite, indicating that manganese species shows highly dispersive with ceria species. The  $\text{H}_2$ -TPR results (Fig. S5†) confirm the interaction between Mn and Ce species in  $\text{CM}_y$  composites. Especially,  $\text{CM}_{20}$  shows excellent redox activity, which can be mainly attributed to the interaction between Ce and Mn species, inducing the changes of the local atomic environment for each element, as detected by the following XPS measurements.

### 3.4 XPS measurements

Fig. 4 shows the Mn 2p, Ce 3d and O 1s XPS spectra of the series of  $\text{CM}_y$  composites, as well as the references  $\text{MnO}_x$  and  $\text{CeO}_2$ . The analysis results of different samples are summarized in Table 1, based on the careful peak fitting procedure. The O 1s XPS spectra of the sample  $\text{CM}_y$  and the references  $\text{MnO}_x$  and  $\text{CeO}_2$  can be deconvoluted into two components after Gaussian fitting, as shown in Fig. 4c, which can be ascribed to lattice oxygen  $\text{O}_{\text{latt}}$  (529.6 eV) and adsorbed oxygen  $\text{O}_{\text{ads}}$  (532.4 eV), respectively. Generally, adsorbed oxygen species always correspond to the numbers of oxygen vacancies,<sup>39</sup> which are beneficial for the activation of gaseous oxygen molecules in the feed gas. The existence of oxygen vacancies in  $\text{CM}_y$  can also be evidently confirmed by the results of Raman spectroscopy analysis (Fig. S6†). Compared with reference  $\text{CeO}_2$ , the main peak in the Raman spectra of  $\text{CM}_y$ , the  $\text{F}_{2g}$  mode of  $\text{CeO}_2$  shows a distinct red-shift from 464 to (433–452)  $\text{cm}^{-1}$ , indicating that the interaction between Mn and Ce disturbed the fluorite-like structure to some extent and resulted in the formation of the oxygen vacancies in the  $\text{CeO}_2$  lattice.<sup>40</sup> It is noting that the peak at 652  $\text{cm}^{-1}$  for  $\text{MnO}_x$  also shifts down to (605–637)  $\text{cm}^{-1}$  for  $\text{CM}_y$  composites, which could also be related to the formation of oxygen vacancies in  $\text{CM}_y$ .<sup>40</sup> Usually, the high ratio of  $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$  indicates a high activity toward oxidation reaction. But in the present work,  $\text{CM}_{20}$ , though with the lowest  $\text{O}_{\text{ads}}/\text{O}_{\text{latt}}$  ratio

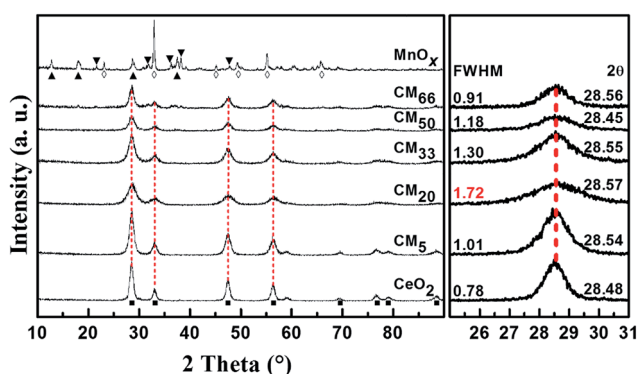


Fig. 2 XRD patterns of different  $\text{CM}_y$  composites and the references  $\text{MnO}_x$  and  $\text{CeO}_2$  (left), (■)- $\text{CeO}_2$ ; (◇)- $\text{Mn}_2\text{O}_3$ ; (▲)- $\text{MnO}_2$ ; (▼)- $\text{Mn}_5\text{O}_8$ ), and the enlarged region between  $25^\circ$  and  $31^\circ$  of the patterns showing the corresponding FWHM values and peak positions of  $2\theta$  (right).



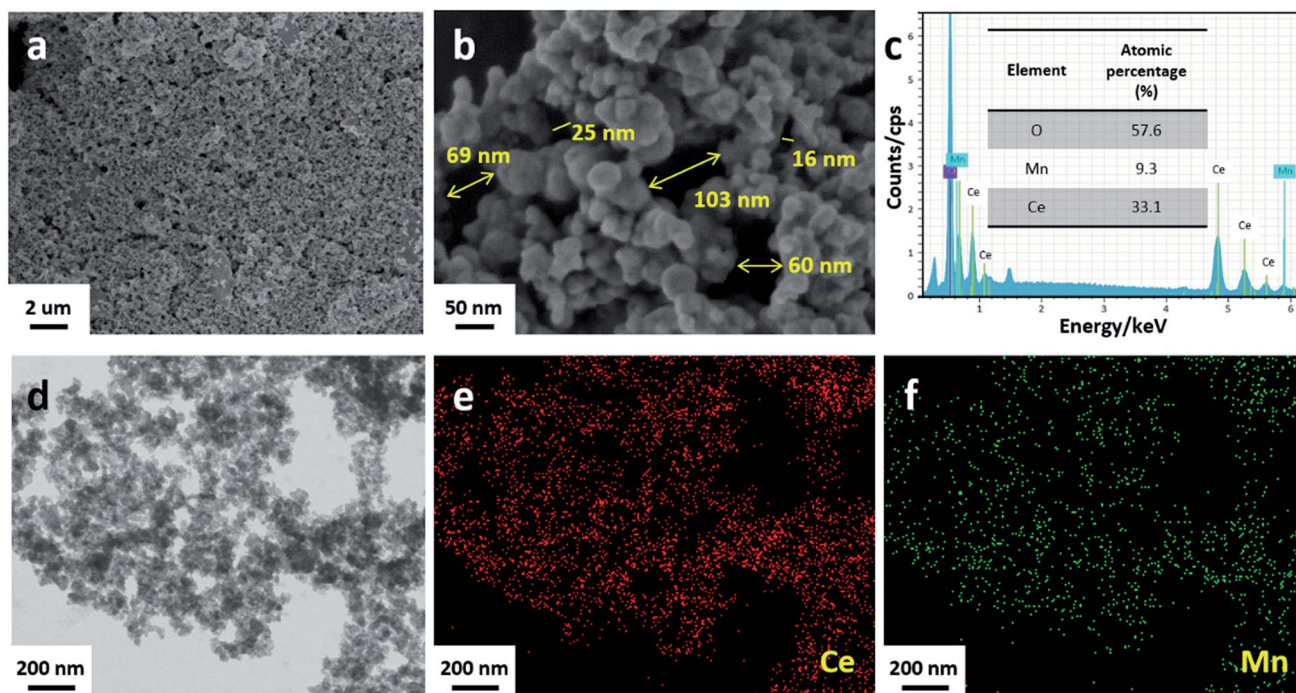


Fig. 3 Low-magnification SEM image (a), high-magnification SEM image (b), EDS spectrum (c), typical TEM image (d) and the element mapping (e and f) of CM<sub>20</sub>.

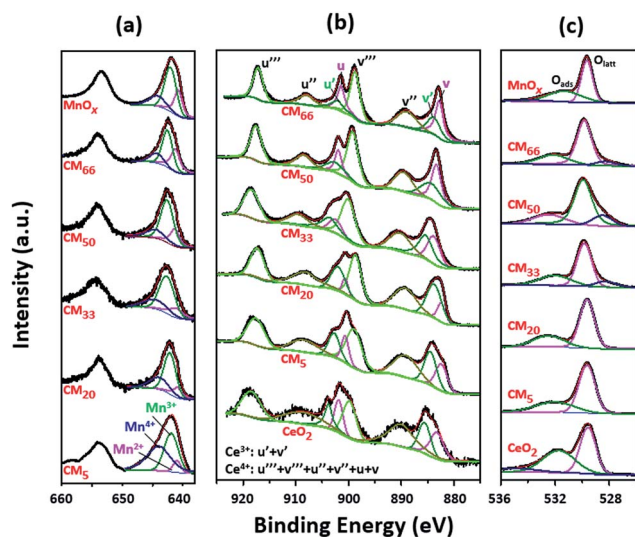


Fig. 4 XPS spectra of (a) Mn 2p, (b) Ce 3d and (c) O 1s for all CM<sub>y</sub> composites and the reference MnO<sub>x</sub> and/or CeO<sub>2</sub>.

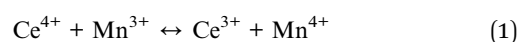
among all the studied catalysts, still shows the highest catalytic activity for soot combustion in NO<sub>x</sub>/O<sub>2</sub>, which suggests that there exists another key factor besides adsorbed oxygen species determining the catalytic activity.

As shown in the Fig. 4 and Table 1, both Mn and Ce species present various valence states. Thereinto, it is found that the ratio of Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) firstly increases and then decreases with the increase of *y* in CM<sub>y</sub>, and the value reaches to a maximum value of 27.6% in CM<sub>20</sub>, which indicates the charge

Table 1 XPS surface composition analysis of CM<sub>y</sub> composites and the references MnO<sub>x</sub> and/or CeO<sub>2</sub>

Sample	O <sub>ads</sub> /(O <sub>ads</sub> + O <sub>latt</sub> ) (%)	Mn <sup>2+</sup> /Mn <sup>3+</sup> /Mn <sup>4+</sup> (%)	Ce <sup>3+</sup> /(Ce <sup>3+</sup> + Ce <sup>4+</sup> ) (%)
MnO <sub>x</sub>	54.9	27.5/52.1/20.3	
CM <sub>66</sub>	33.3	35.2/48.7/16.1	17.3
CM <sub>50</sub>	31.1	22.1/56.9/21.1	19.2
CM <sub>33</sub>	30.5	20.1/58.5/21.3	24.9
CM <sub>20</sub>	21.2	16.0/54.9/29.0	27.6
CM <sub>5</sub>	27.7	8.0/56.8/35.1	22.0
CeO <sub>2</sub>	46.6		18.2

transfer between Mn and Ce within the interface (eqn (1)), as supported by the previous reports demonstrating negative charge transfer either from Mn to Ce or from Ce to Mn.<sup>41–45</sup> Such a charge transfer will lead to the strong interaction between Ce and Mn species and thus the formation of uniform nanoparticles.<sup>46</sup> This strong interaction between Mn and Ce can also be reflected in the results of H<sub>2</sub>-TPR profiles shown in Fig. S5,† in which, all of the CM<sub>y</sub> composites especially CM<sub>20</sub> and CM<sub>33</sub> show much lower reduction peak temperature than that for either MnO<sub>x</sub> or CeO<sub>2</sub>. Additionally, it is reported that the Mn<sup>4+</sup> and Ce<sup>3+</sup> can absorb and activate NO and O<sub>2</sub>,<sup>47,48</sup> thus the Mn<sup>4+</sup> and Ce<sup>3+</sup> cations could serve as active sites for the catalytic soot combustion in NO<sub>x</sub>/O<sub>2</sub> atmosphere, by promoting the formation of NO<sub>2</sub>.



To further verify the role of  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations in the catalytic soot oxidation, a parameter “ $\Omega$ ” (defined in eqn (2)) was introduced to quantify the concentration of  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations in the  $\text{CM}_y$  composites.

$$\Omega = a \times b \quad (2)$$

Where  $a = (1 - y)[\text{Ce}^{3+}/(\text{Ce}^{3+} + \text{Ce}^{4+})]$ ,  $b = y[\text{Mn}^{4+}/(\text{Mn}^{2+} + \text{Mn}^{3+} + \text{Mn}^{4+})]$ , and  $y$  is that in  $\text{CM}_y$ . Moreover, the relationship between “ $\Omega$ ” value and the catalytic activity over the different catalysts  $\text{CM}_y$  are shown in Fig. 5. It is found that for the  $\text{CM}_y$  composites, the larger  $\Omega$  value is, the higher catalytic activity is, which confirms the role of  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations as active sites for catalytic soot combustion in  $\text{NO}_x/\text{O}_2$  over  $\text{CM}_y$  composites. Nevertheless, the sample  $\text{CM}_{66}$  seems an exception with a lower  $\Omega$  value, showing higher catalytic activity than  $\text{CM}_{50}$ , which can be ascribed to the higher specific surface area and pore volume of  $\text{CM}_{66}$  ( $72 \text{ m}^2 \text{ g}^{-1}$  and  $0.22 \text{ cm}^3 \text{ g}^{-1}$ , Table S2†) than those of  $\text{CM}_{50}$  ( $53 \text{ m}^2 \text{ g}^{-1}$  and  $0.11 \text{ cm}^3 \text{ g}^{-1}$ , Table S2†).

### 3.5 SEM and TEM measurements for $\text{CM}_{33}$

It is worth noting that, compared with  $\text{CM}_{20}$ ,  $\text{CM}_{33}$  shows a little lower catalytic activity and  $\Omega$  value, and similar specific surface area but significantly lower pore volume. Therefore, the TEM and SEM analyses for  $\text{CM}_{33}$  were further performed, as shown in Fig. 6. It can be found that very different from the homogeneous morphology of  $\text{CM}_{20}$  particles shown in Fig. 3,  $\text{CM}_{33}$  shows some complex morphology in addition to the highly dispersive particles, such as micro-flakes (1 in Fig. 6c) and microspheres (3 in Fig. 6c). These two kinds of morphologies can also be found in the Ce-rich samples ( $\text{CeO}_2$  and  $\text{CM}_5$  in Fig. S3†), and the Mn-rich samples ( $\text{CM}_{50}$ ,  $\text{CM}_{66}$  and  $\text{MnO}_x$  in Fig. S3†), respectively. Apparently, either the micro-flakes or the microsphere morphology in  $\text{CM}_{33}$  lacks the porous structure, thus leading to the lower pore volume than  $\text{CM}_{20}$  (Table S2†), which can strongly affect the efficient contact between catalyst and soot

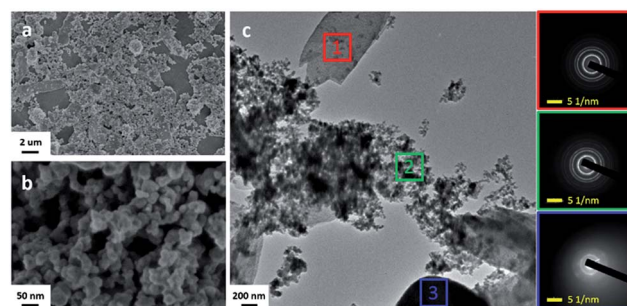


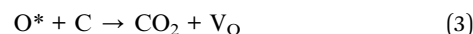
Fig. 6 Low-magnification SEM image (a), high-magnification SEM image (b), TEM image (c) of  $\text{CM}_{33}$ , and the corresponding SAED patterns to the different areas in (c).

particles and decrease the activity for soot oxidation. Nevertheless, the main component in  $\text{CM}_{33}$  still presents similar size and chemical composition (Fig. 6b, 2 in Fig. 6c and S7†) to  $\text{CM}_{20}$  particles (Fig. 3), thus it remains higher catalytic activity than other reference samples. Therefore, it is reconfirmed that the homogeneous particles morphology with hierarchically porous structure is one of the key factors in the catalytic process of soot oxidation.

Overall, the catalytic activity for soot oxidation in  $\text{NO}_x/\text{O}_2$  atmosphere can be ascribed to the following two aspects: (1) abundant  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations (large  $\Omega$  value) serve as active sites by promoting  $\text{NO}_2$  production, *e.g.*,  $\text{CM}_{20}$  with the largest  $\Omega$  value ( $\Omega = 128$ ) shows the best activity toward the soot oxidation. (2) The high surface area and pore volume as well as the typical morphology of the particles with hierarchically porous structure could improve the dispersion of active species and soot diffusion, *e.g.*,  $\text{CM}_{66}$  with a lower  $\Omega$  value ( $\Omega = 62$ ) exhibits a relatively high activity for soot oxidation due to its high specific surface area and pore volume.

### 3.6 A possible catalytic mechanism for soot oxidation

Based on the above results and analyses, a possible mechanism for the catalytic soot combustion in  $\text{NO}_x/\text{O}_2$  over the sample  $\text{CM}_{20}$  was proposed, as shown in Scheme 1. In this catalytic reaction, the efficient contact between the catalyst and soot, and the abundant active  $\text{Mn}^{4+}$ - $\text{Ce}^{3+}$  species are two crucial issues determining the excellent catalytic performance. Generally, soot combustion over catalyst in  $\text{NO}_x/\text{O}_2$  atmospheres is believed to follow two different pathways:<sup>49</sup> (i) direct soot combustion by surface active oxygen species, (ii) NO-aided soot combustion. In Route (i), oxygen species absorbed and activated by oxygen vacancies ( $\text{V}_\text{O}$ ) on the catalyst surface can directly oxidize soot into  $\text{CO}_2$  (reaction (3), where  $\text{O}^*$  is the active oxygen species).<sup>50</sup>



While in Route (ii), the NO-aided soot combustion can be expressed as the following reactions:

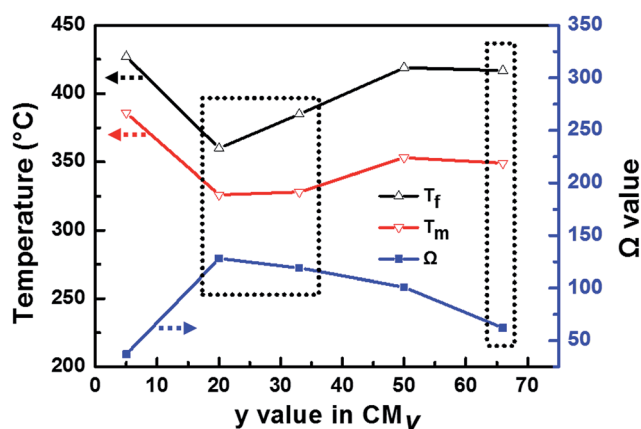
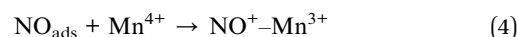
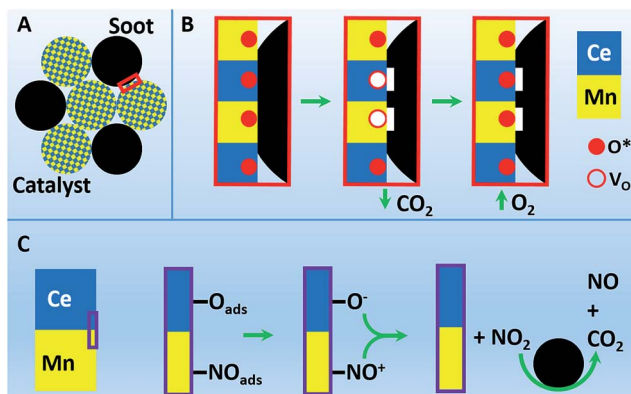
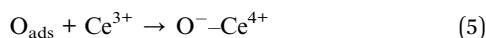


Fig. 5 The different characteristic temperatures ( $T_m$  and  $T_f$ ) and values of “ $\Omega$ ” as a function of  $y$  in  $\text{CM}_y$ . Reaction conditions for catalytic soot combustion: 500 ppm NO and 10%  $\text{O}_2$  in  $\text{N}_2$  with a total flow of  $200 \text{ mL min}^{-1}$ , mass of soot–catalyst–silica is 10–100–1000 mg, under loose contact mode.





Scheme 1 Schematic illustration of (A) the sufficient mixing of  $\text{CM}_{20}$  and soot particles, and the possible pathways of soot combustion on  $\text{CM}_{20}$  in  $\text{NO}_x/\text{O}_2$ : (B) Route (i): direct soot combustion by surface active oxygen species; (C) Route (ii): NO-aided soot combustion.



As supported by previous reports, it can be rationally deduced that the abundant  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations in  $\text{CM}_{20}$  play different roles in the catalytic process. Therein,  $\text{Mn}^{4+}$  could adsorb and activate NO into active species  $\text{NO}^+$ , as shown in reaction (4);<sup>47</sup> while  $\text{Ce}^{3+}$  could activate the adsorbed oxygen  $\text{O}_{\text{ads}}$  into  $\text{O}^-$  (reaction (5)).<sup>48</sup> Such resultant  $\text{NO}^+$  and  $\text{O}^-$  species will react with each other to form  $\text{NO}_2$  at the interface between Ce and Mn oxides (reaction (6)),<sup>51</sup> meanwhile, the produced  $\text{Ce}^{4+} - \text{Mn}^{3+}$  will react through reaction (1) to recover the active site  $\text{Ce}^{3+} - \text{Mn}^{4+}$ , thus completing the catalysis cycle. Then in

## 4. Conclusions

In summary, a facile co-precipitation method has been adopted to prepare a series of  $\text{MnO}_x - \text{CeO}_2$  composites for the catalytic oxidation of soot in the simulated diesel emission. Thereinto, the optimized  $\text{CM}_{20}$  shows the highest catalytic activity ( $T_f = 360$  °C), under loose contact mode. The excellent catalytic activity can be attributed to its uniform particle morphology with hierarchically porous structure and the rich active  $\text{Mn}^{4+}$  and  $\text{Ce}^{3+}$  cations resulting from the suitable doping amount of Mn, which greatly accelerate soot oxidation in  $\text{NO}_x/\text{O}_2$ . A possible mechanism was proposed to interpret the role of  $\text{Mn}^{4+} - \text{Ce}^{3+}$  species as well as the active oxygen species in the catalytic process of soot combustion in  $\text{NO}_x/\text{O}_2$ . The  $\text{MnO}_x - \text{CeO}_2$  composites prepared by this low-cost and easily-scalable method could find the promising practical application in the catalytic removal of soot in the diesel exhaust.

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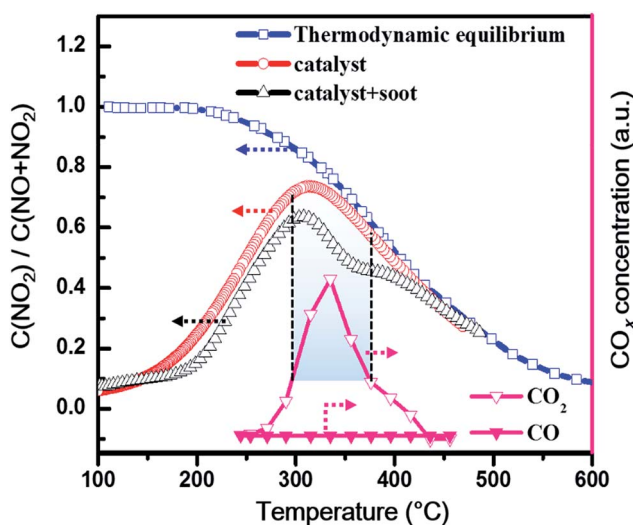
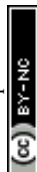


Fig. 7 The temperature-programmed oxidation of NO over  $\text{CM}_{33}$  with or without soot under loose contact mode. Reaction conditions: 500 ppm NO and 10%  $\text{O}_2$  in  $\text{N}_2$  with a total flow of  $200 \text{ mL min}^{-1}$ , the mass of (soot-)catalyst-silica is (10-)100–1000 mg.



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