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Soot combustion performance and H₂-TPR study on ceria-based mixed oxides

SHENG Yeqin, ZHOU Ying, LU Hanfeng*, ZHANG Zekai, CHEN Yinfei

College of Chemical Engineering and Materials Science, Research Institute of Catalytic Reaction Engineering, Zhejiang University of Technology, Hangzhou 310014, Zhejiang, China

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ABSTRACT

Ceria (CeO₂) catalysts doped with different metal ions were prepared by sol-gel or impregnation methods, and their catalytic activity for soot combustion was evaluated by thermogravimetry. Temperature-programmed reduction was used to investigate the influence of their redox properties on soot combustion performance. The results indicate that the oxidation temperature of soot can be significantly reduced using catalysts containing transition metals, which provide increased surface and lattice oxygen compared with undoped CeO₂. The ability of each catalyst to deliver active oxygen at low temperature (200–400 °C) plays an important role in determining catalytic performance. However, incorporation of structure promoter, alkali metals, and alkaline earth metals increase the delivery of active oxygen only at moderate temperature (above 400 °C), which accelerate the combustion rate of soot.

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1. Introduction

The extensive use of diesel engines that generate particulate matter (PM), whose main component is soot, poses serious risks to human health and pollutes the atmosphere [1], so removal of PM is a topic of ongoing research. Various emission-reduction technologies have been developed. Besides improving engines and fuel quality, filtering followed by catalytic oxidation is considered to be the most direct and efficient solution to reduce PM [2].

Ceria (CeO₂) is of great significance as a basic catalytic material for soot combustion because of its appreciable oxygen storage capacity (OSC) and excellent redox properties [3]. However, the temperature window of soot oxidation under pure ceria is much higher than the temperature of diesel exhaust (< 400 °C), and significant deactivation of CeO₂ occurs at high temperature because the particles are sintered. In recent

years, doping CeO₂ with transition, rare earth, or alkali metals to form ceria-based solid solutions has proved to be a convenient and effective approach to improve the catalytic activity and thermal stability of CeO₂ [4–8]. The structural features and physicochemical characteristics, especially the redox capacity, of CeO₂ are inevitably changed by doping. In general, redox reactions follow the Mars-van Krevelen mechanism; that is, soot oxidation is realized in the redox cycle of metallic oxides providing there is sufficient soot-catalyst contact [9]. The most important factor associated with soot combustion by redox reaction is the ability of the catalyst to deliver active oxygen to the solid carbon reactant in an appropriate temperature range [6,10].

During temperature-programmed reduction (H₂-TPR) process, metallic cations with high valence state and lattice oxygen ions are reduced by H₂ to form ions with low valence state or metallic atoms and H₂O, respectively. Therefore, both the spe-

* Corresponding authors. Tel: +86-571-88320767; Fax: +86-571-88320767; E-mail: luhf@zjut.edu.cn

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cies and amount of active oxygen, particularly the mobility of lattice oxygen, can be analyzed qualitatively and quantitatively by H₂-TPR measurement of ceria-based mixed oxides. Such a study will have profound significance for research on the catalytic combustion of soot. Accordingly, in the present study, CeO₂ was doped with transition, structure promoter, alkali and alkaline earth metals and the redox properties of the resulting materials were characterized by H₂-TPR. The purpose of this work is to gain further insight into the influence of the distribution of active oxygen in CeO₂-based materials on soot combustion performance.

2. Experimental

2.1. Catalyst preparation

Ceria-based mixed oxides doped with transition and structure promoter metals, or modified with alkali or alkaline earth metals were prepared by citric acid-assisted sol-gel or impregnation methods, respectively, using the corresponding nitrates as precursors.

CeO₂ doped with transition metals were formed by the following process. Cr(NO₃)₃·9H₂O, Mn(NO₃)₂, Fe(NO₃)₃·9H₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, or Cu(NO₃)₂·3H₂O was dissolved in a solution of Ce(NO₃)₃·6H₂O to give a molar ratio of 0.8:0.2. Two molar equivalents of citric acid were added as a complexing agent. Polyglycol (10 wt% to that of citric acid) was then added. Each solution was stirred and heated until a porous gel formed. Each gel was dried at 110 °C for 12 h, decomposed at 300 °C for 1 h, and then calcined at 500 °C for 3 h to obtain the catalysts (denoted Ce_{0.8}T_{0.2}O₂).

CeO₂ doped with structure promoter metals were formed by the following process. Ce(NO₃)₃·6H₂O and Zr(NO₃)₄·3H₂O, Y(NO₃)₃·6H₂O, or La(NO₃)₃·6H₂O were mixed to form solutions with a molar ratio of 0.8:0.2. The resulting catalysts are labeled as Ce_{0.8}R_{0.2}O₂.

Loading of alkali or alkaline earth metals on CeO₂: These catalysts are designated 10%A-CeO₂ (A = Na, K, Mg, Ba) and contain a molar ratio of A/Ce of 10%.

MnO_x-CeO₂ mixed oxides with different molar ratios were synthesized following the sol-gel method described above. The resulting powders were calcined at 500 °C for 3 h to form catalysts denoted as Ce_{1-x}Mn_xO₂ (x = 0.2, 0.4, 0.6, 0.8, 1.0).

2.2. Catalytic activity measurement

The oxidation of soot (Printex-U provided by Degussa) by the catalysts was studied in a thermogravimetric (TG) analyzer (Netzsch STA 409PC, Germany) [3,6]. Activity measurements were obtained under 'tight contact' conditions, where soot-catalyst mixtures with a weight ratio of 1:10 were ground in an agate mortar for 10 min. Such conditions allow the activity of the catalysts under optimum conditions to be investigated. Oxidation experiments involved heating each mixture (about 10 mg) at a rate of 10 °C/min from 25 to 650 °C under a flow of 10% O₂-90% N₂ (50 ml/min).

Catalytic activity was evaluated in three ways: (a) the igni-

tion temperature of soot (T_i , the extrapolated starting point of a TG curve); (b) the temperature at which soot oxidation proceeded at the highest rate (T_m , the maximum of a DTG curve); (c) the burnout temperature of soot (T_f , the extrapolated end point of a TG curve).

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were determined by a diffractometer (ARLS CINTAG X'TRA) using nickel-filtered Cu K α radiation and were recorded at 0.02° intervals in the range of 10° ≤ 2θ ≤ 80° at a voltage of 45 kV and current of 30 mA.

The specific surface areas of samples were determined from N₂ adsorption isotherms measured at -196 °C using the Brunauer-Emmett-Teller (BET) method and a micropore system (ASAP 2020M, Micromeritics, USA). Samples were pretreated under vacuum at 300 °C for 2 h prior to measuring isotherms.

H₂-TPR experiments were performed on a chemisorption analyzer (FINESORB-3010E, Fantai, China). Each sample (200 mg of fresh catalyst) was pretreated by calcination at 200 °C for 1 h and subsequently cooled to 100 °C under an Ar flow (30 ml/min). Then, a 5% H₂-95% Ar flow (30 ml/min) was flowed over the catalyst bed at 100 °C for 20 min, followed by heating at a rate of 10 °C/min up to 750 °C. Finally, the catalyst was cooled under an Ar flow (30 ml/min). The consumption of H₂ was monitored by a thermal conductivity detector (TCD) operating at 60 °C and 60 mA.

3. Results and discussion

3.1. CeO₂ doped with transition metals

3.1.1. Texture of catalysts

Powder XRD patterns of CeO₂ doped with different transition metals are shown in Fig. 1(a). The lattice constants and mean crystallite sizes of CeO₂ in the samples were calculated by Bragg law and Scherrer equation, respectively (Table 1). In the samples, CeO₂ exhibits the typical reflections of a cubic fluorite structure. In general, shrinkage of the lattice is expected when metal ions with a smaller ionic radius than Ce are incorporated into CeO₂. However, no obvious changes of the cell parameters and lattice expansion are observed for Cu and Co dopants, respectively. The lower specific surface areas of Ce_{0.8}Cu_{0.2}O₂ and Ce_{0.8}Co_{0.2}O₂ catalysts than that of CeO₂ further confirm that Co and Cu are mainly dispersed on the surface of CeO₂ without forming ceria-based solid solutions. Two diffraction peaks attributed to CuO observed in the XRD pattern of Ce_{0.8}Cu_{0.2}O₂ suggest the presence of large CuO_x particles, which is consistent with related literature [11–14]. CeO₂ catalysts doped with Cr, Mn, Fe, and Ni only show the diffraction peaks of CeO₂, which are all shifted slightly to a higher diffraction angle, especially for the Ce_{0.8}Mn_{0.2}O₂ catalyst. This indicates that ceria-based solid solutions are formed by partial replacement of Ce⁴⁺ with these smaller transition metal cations, decreasing the lattice constant of CeO₂ (Table 1). Doping CeO₂ with transition metals

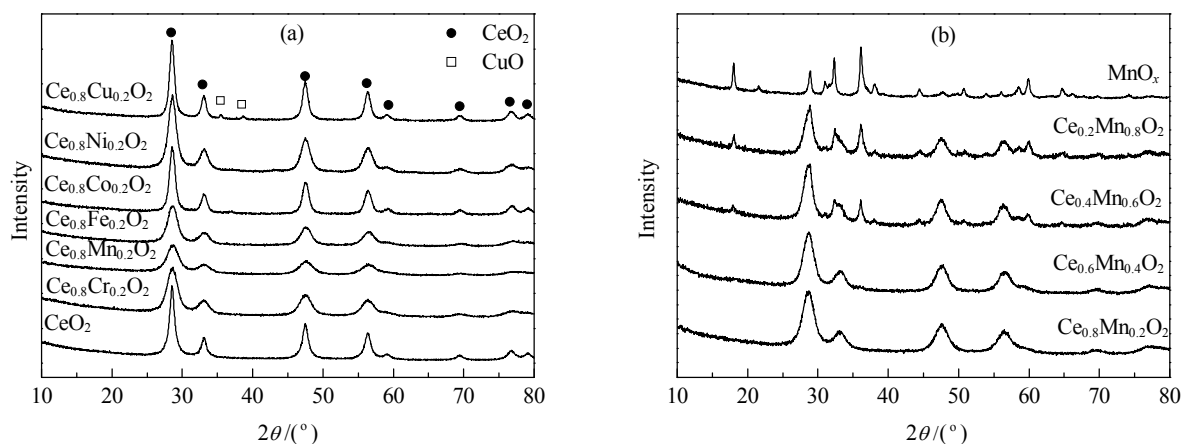


Fig. 1. XRD patterns of Ce-based catalysts doped with different transition metals. (a) $\text{Ce}_{0.8}\text{T}_{0.2}\text{O}_2$ ($\text{T} = \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{Cu}$); (b) $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0$).

also reduce crystallite size and increase surface area. For example, the crystallite size of $\text{Ce}_{0.8}\text{Mn}_{0.2}\text{O}_2$ decreases from 11.7 to 7.8 nm, accompanied by an improvement of A_{BET} from 29.7 to 77.4 m^2/g compared with those of CeO_2 .

Mn-Ce solid solutions are considered to possess a structure that promotes catalytic combustion of soot [4,12,14], so CeO_2 catalysts doped with different amounts of Mn were also characterized by XRD. As seen from Fig. 1(b), as the content of Mn is increased, the single diffraction peak of CeO_2 is transformed into several sharper peaks ascribed to MnO_x . Kang et al. [15] reported the solubility limit of Mn cations in CeO_2 is 5–10 mol% depending on the preparation procedure, and excess Mn ions are dispersed on the surface of CeO_2 as MnO_x . Therefore, it is reasonable to suggest that MnO_x clusters are dispersed on the ceria surface for $x = 0.2$ and 0.4, although only typical diffraction peaks of CeO_2 are observed in the XRD patterns. Obvious MnO_x phases are detected in the XRD patterns of $\text{Ce}_{0.4}\text{Mn}_{0.6}\text{O}_2$ and $\text{Ce}_{0.2}\text{Mn}_{0.8}\text{O}_2$ with increased Mn content, which is attributed to the increase of crystallite size and reduction of specific surface area caused by the accumulation of numerous MnO_x particles as the proportion of solid solution in the catalysts decreases.

3.1.2. H_2 -TPR characterization and performance of catalysts for soot combustion

H_2 -TPR profiles of $\text{Ce}_{0.8}\text{T}_{0.2}\text{O}_2$ catalysts are illustrated in Fig.

2(a). Pure CeO_2 only shows a reduction peak at 453 °C, which can be assigned to the reduction of Ce^{4+} to Ce^{3+} . Upon doping with transition metals, the reduction peaks of the samples shift to lower temperature and possess larger peak areas, indicating a significant improvement in reducibility. It is noted that the redox properties of CeO_2 are greatly enhanced by introducing Co or Cu; in particular, $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ shows a major reduction peak at 196 °C with a shoulder at 150 °C, despite it not forming a solid solution. In agreement with the literature [16], the reduction peak temperature of CuO is significantly lowered upon addition of CeO_2 because of H_2 spillover, coupled with an improvement of OSC. However, the soot ignition temperature ($T_i = 383$ °C, Table 2) of the $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ catalyst is the highest of the transition metal-doped catalysts. It has not been reported that soot can be activated to ignite below 200 °C, even with the aid of noble metals catalysts, which may be attributed to the very high Arrhenius activation energies required in soot oxidation [17]. It seems therefore that the surface oxygen provided by $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ at 200 °C does not have a direct beneficial effect on the ignition temperature of soot. Compared with those of bare Co_3O_4 , which is the main form of Co in Co-Ce mixed oxides [18], the reduction peaks of $\text{Ce}_{0.8}\text{Co}_{0.2}\text{O}_2$ are shifted to a lower temperature [19]. In addition, $\text{Ce}_{0.8}\text{Co}_{0.2}\text{O}_2$ displays good activity for soot combustion, implying the ability to deliver oxygen is increased through a synergistic effect between highly dispersed Co_3O_4 microcrystals and CeO_2 .

Table 1

Textural properties of $\text{Ce}_{0.8}\text{T}_{0.2}\text{O}_2$ and $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ catalysts.

Sample	$2\theta/(\text{°})$	Lattice constant (nm)	Crystallite size (nm)	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Ionic radius (nm)
CeO_2	28.5738	0.5406	11.7	29.7	Ce^{3+} : 0.103; Ce^{4+} : 0.092
$\text{Ce}_{0.8}\text{Cr}_{0.2}\text{O}_2$	28.6764	0.5388	8.1	50.8	Cr^{2+} : 0.084; Cr^{3+} : 0.069
$\text{Ce}_{0.8}\text{Fe}_{0.2}\text{O}_2$	28.7685	0.5371	7.8	36.6	Fe^{2+} : 0.074; Fe^{3+} : 0.064
$\text{Ce}_{0.8}\text{Co}_{0.2}\text{O}_2$	28.5407	0.5413	10.4	7.9	Co^{2+} : 0.072; Co^{3+} : 0.063
$\text{Ce}_{0.8}\text{Ni}_{0.2}\text{O}_2$	28.6284	0.5396	9.0	44.2	Ni^{2+} : 0.069
$\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$	28.5985	0.5402	11.4	16.9	Cu^+ : 0.096; Cu^{2+} : 0.072
$\text{Ce}_{0.8}\text{Mn}_{0.2}\text{O}_2$	28.8008	0.5365	7.8	77.4	
$\text{Ce}_{0.6}\text{Mn}_{0.4}\text{O}_2$	28.6849	0.5386	8.5	24.0	Mn^{2+} : 0.080
$\text{Ce}_{0.4}\text{Mn}_{0.6}\text{O}_2$	28.8824	0.5349	9.6	21.6	Mn^{3+} : 0.066
$\text{Ce}_{0.2}\text{Mn}_{0.8}\text{O}_2$	28.9163	0.5344	10.5	11.5	Mn^{4+} : 0.060
MnO_x	36.0937	0.9403	34.2	9.5	

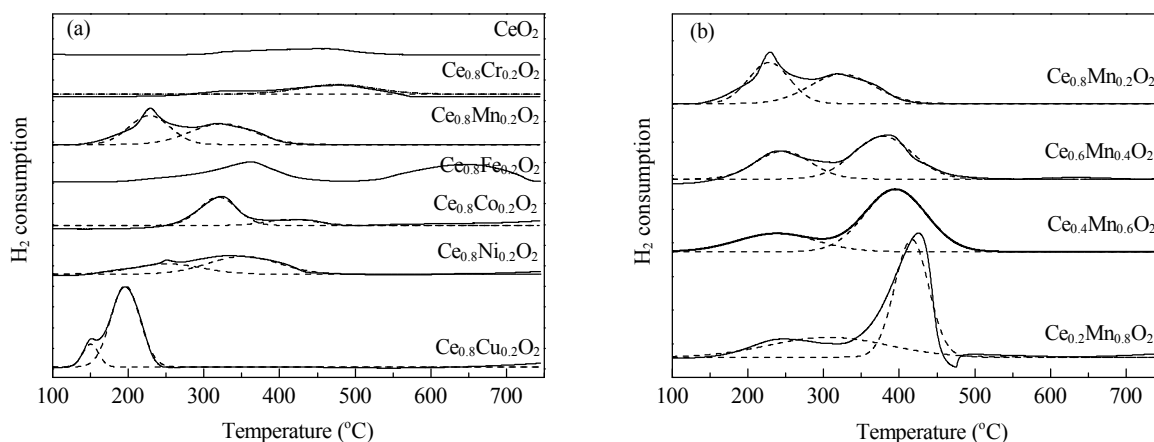


Fig. 2. H₂-TPR profiles of Ce-based catalysts doped with different transition metals. (a) Ce_{0.8}T_{0.2}O₂ (T = Cr, Mn, Fe, Co, Ni, Cu); (b) Ce_{1-x}Mn_xO₂ (x = 0.2, 0.4, 0.6, 0.8, 1.0).

Doping of ceria with transition metals such as Cr, Mn, Fe, and Ni increases its OSC because ceria-based solid solutions form, causing marked variation of redox properties, which affect soot combustion. The small reduction peak at 346 °C for the Cr-doped catalyst suggests that little surface oxygen is available, which reduces T_i from 397 to 375 °C. However, a larger value of ΔT ($T_f - T_i$, the difference between the burnout temperature and ignition temperature of soot) is obtained, indicating a decrease in the rate of soot combustion, which is heavily influenced by the reduced bulk oxygen provided by Ce_{0.8}Cr_{0.2}O₂. For the Fe-Ce mixed oxide, the two observed reduction peaks are generally ascribed to the reduction of Fe₂O₃→Fe₃O₄ and Fe₃O₄→FeO [20]. The soot burnout temperature increases to 502 °C because of the large amount of lattice oxygen released at high temperature by this catalyst, although the soot ignition temperature is the same as that of the first reduction peak (360 °C). Comparison of these transition metal-doped CeO₂ catalysts reveals that only the two reduction peaks of the Ce_{0.8}Mn_{0.2}O₂ catalyst, which are associated with the reduction of Mn₂O₃→Mn₃O₄ and Mn₃O₄→MnO [21], fall in the temperature range where the combustion of soot can be catalyzed. In particular, the first sharp reduction peak shows a high migration rate of surface oxygen, which leads to a much lower soot ignition temperature of 347 °C. Hence, the incorporation of Mn into the ceria lattice greatly increases the density of active oxygen species with high mobility at low temperature,

contributing to the superior catalytic activity of Ce_{0.8}Mn_{0.2}O₂ compared with the other catalysts.

In view of the normal diesel exhaust temperature range of 200–400 °C [22], the oxygen release capacity of each catalyst in this temperature range is an important factor affecting soot combustion performance. The H₂ consumption of Ce_{0.8}T_{0.2}O₂ catalysts from 200–400 °C, which was calculated by integrating the corresponding peak areas with that of a standard sample (CuO), is shown in Fig. 3. A positive correlation was found between the rate of soot combustion and the amount of active

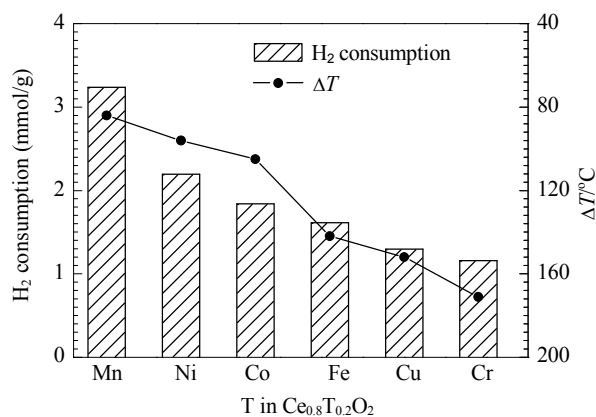


Fig. 3. H₂ consumption at 200–400 °C and ΔT ($T_f - T_i$) for soot combustion of Ce_{0.8}T_{0.2}O₂ sample.

Table 2

H₂-TPR characterization and catalytic performance for soot combustion by Ce_{0.8}T_{0.2}O₂ and Ce_{1-x}Mn_xO₂ catalysts.

Sample	Temperature of peak and H ₂ consumption (H ₂ -TPR)				T_i /°C	T_m /°C	T_f /°C
	Peak 1		Peak 2				
	T /°C	$n(\text{H}_2)$ /(mmol/g)	T /°C	$n(\text{H}_2)$ /(mmol/g)			
CeO ₂	453	0.795	—	—	397	501	566
Ce _{0.8} Cr _{0.2} O ₂	346	0.750	476	1.295	375	490	546
Ce _{0.8} Fe _{0.2} O ₂	360	1.890	638	2.055	360	463	502
Ce _{0.8} Co _{0.2} O ₂	319	1.660	416	0.315	370	418	475
Ce _{0.8} Ni _{0.2} O ₂	251	0.865	352	1.655	380	433	476
Ce _{0.8} Cu _{0.2} O ₂	150	0.520	196	3.355	383	449	535
Ce _{0.8} Mn _{0.2} O ₂	228	1.785	317	1.850	347	389	431
Ce _{0.6} Mn _{0.4} O ₂	240	1.235	384	2.265	381	416	486
Ce _{0.4} Mn _{0.6} O ₂	241	1.320	400	2.935	405	452	506
Ce _{0.2} Mn _{0.8} O ₂	250	1.890	426	3.220	426	495	557

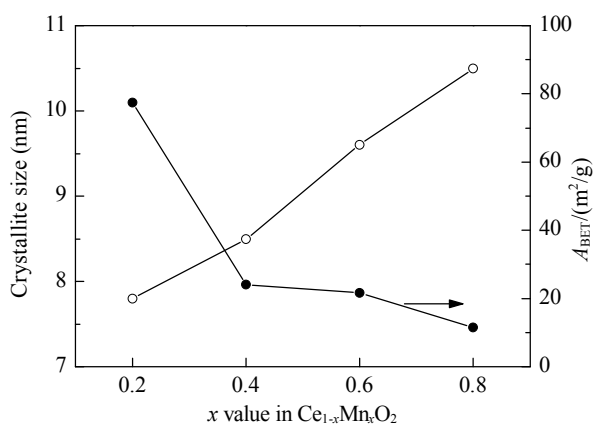


Fig. 4. Distribution of crystallite size and surface area of Ce_{1-x}Mn_xO₂ catalysts.

oxygen released by the samples between 200 and 400 °C because ΔT increased gradually as the amount of H₂ consumed decreased. As stated above, the combination of Co, Cu, and CeO₂ mainly promotes the generation of surface oxygen, while ceria-based solid solutions formed by doping with Cr, Mn, Fe, and Ni greatly accelerate the release of lattice oxygen under tight soot-catalyst contact. Therefore, the high catalytic activity of these mixed oxides shows a marked dependence on the synergy of these two types of active oxygen species at low temperature.

An inverse relationship was found between the crystallite size and surface area for Ce_{1-x}Mn_xO₂ catalysts (Fig. 4), which are reported as the transition metal-doped CeO₂ catalysts with the highest low-temperature activity for soot oxidation. That is, the catalytic activity of these samples increases with increasing surface area and decreasing crystallite size. It is expected that crystallite size and surface area strongly affect the activity of Ce_{1-x}Mn_xO₂ because they change both the interaction between the soot and catalyst and the delivery of oxygen. The influence of Mn doping levels on the redox properties of Ce_{1-x}Mn_xO₂ is presented in Fig. 2(b). The two reduction peaks of Ce_{1-x}Mn_xO₂ below 450 °C progressively shift to higher temperature as x increases: the area of the first peak is gradually reduced to form a flatter shape, in contrast to the second one. Figure 5 also in-

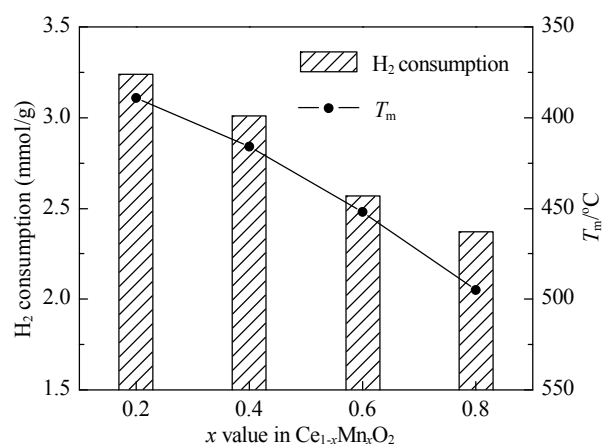


Fig. 5. Distribution of H₂ consumption at 200–400 °C and T_m for Ce_{1-x}Mn_xO₂ catalysts.

dicates that an increase in Mn doping levels leads to a decrease in H₂ consumption by the samples between 200 and 400 °C. This observation agrees with the reduction of T_m, the temperature at which soot combusts at the highest rate. It can be concluded that the high low-temperature activity of the Ce_{0.8}Mn_{0.2}O₂ catalyst is related to its small crystallite size, large surface area, and especially the high availability of active oxygen between 200 and 400 °C.

3.2. CeO₂ catalysts of modified by structure promoter, alkali and alkaline earth metals

3.2.1. Texture of catalysts

Powder XRD patterns of Ce_{0.8}R_{0.2}O₂ and 10%A-CeO₂ catalysts are displayed in Fig. 6. The change of lattice constants listed in Table 3 confirms the formation of solid solutions caused by the substitution of Ce⁴⁺ with different structure promoter, alkali and alkaline earth metal cations. XRD peaks shift to lower angles for Ce_{0.8}La_{0.2}O₂ and higher ones for Ce_{0.8}Zr_{0.2}O₂ and Ce_{0.8}Y_{0.2}O₂, reflecting the order of their ionic radii of La^{x+} > Ce^{x+} > Y^{x+} > Zr^{x+}. In addition, the surface area is significantly increased by doping with Zr but decreased for Ce_{0.8}Y_{0.2}O₂ and Ce_{0.8}La_{0.2}O₂ because the metal oxides of Y and La

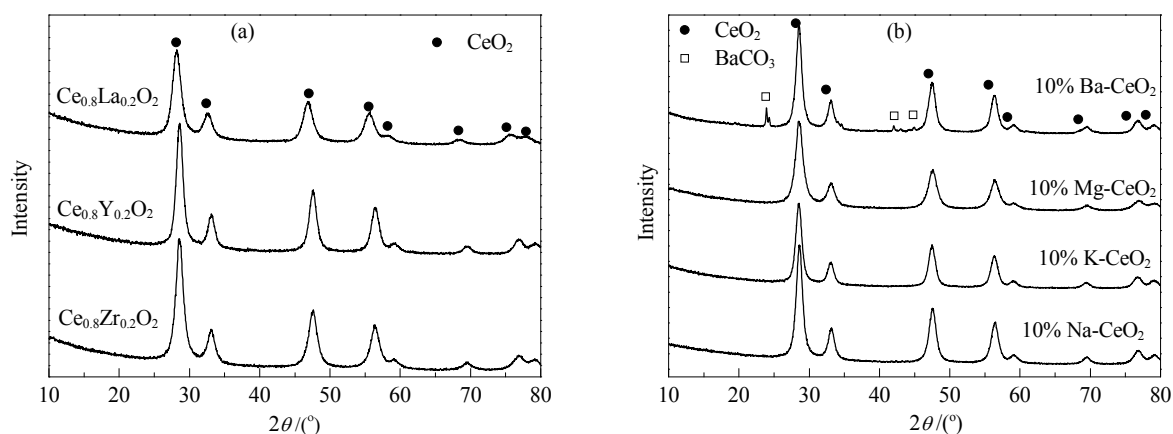


Fig. 6. XRD patterns of Ce-based catalysts doped with different structure promoter, alkali and alkaline earth metals. (a) Ce_{0.8}R_{0.2}O₂ (R = Zr, Y, La); (b) 10%A-CeO₂ (A = Na, K, Mg, Ba).

Table 3Textural properties of $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_2$ and 10%A-CeO₂ catalysts.

Sample	$2\theta/(\circ)$	Lattice constant (nm)	Crystallite size (nm)	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Ionic radius (nm)
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	28.9660	0.5335	8.4	81.0	Zr^{4+} : 0.08
$\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$	28.6725	0.5389	8.7	12.9	Y^{3+} : 0.088
$\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_2$	28.3340	0.5452	8.7	13.0	La^{3+} : 0.106
10%Na-CeO ₂	28.7334	0.5377	9.7	68.4	Na^+ : 0.095
10%K-CeO ₂	28.7374	0.5376	9.9	66.9	K^+ : 0.133
10%Mg-CeO ₂	28.7636	0.5372	9.3	16.4	Mg^{2+} : 0.065
10%Ba-CeO ₂	28.6542	0.5392	10.5	12.8	Ba^{2+} : 0.135

are mainly dispersed on the surface, as Y^{3+} and La^{3+} are too large to enter the CeO₂ lattice. Meanwhile, the crystallite size of CeO₂ is also reduced by modification with alkali and alkaline earth metal cations. Introducing Na⁺ and K⁺ caused the surface area of CeO₂ to increase because of their strong surface mobility [23]. Conversely, addition of Mg²⁺ and Ba²⁺, which can generate carbonate species such as BaCO₃ that can cover the surface of solid solutions, were found on the 10%Ba-CeO₂ catalyst [24].

3.2.2. H₂-TPR characterization and performance of catalysts for soot combustion

H₂-TPR profiles of the $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_2$ catalysts are presented in Fig. 7(a). The reduction peaks of all of the samples doped with structure promoter metals shift to a higher temperature with larger peak areas, revealing the abundance of lattice oxygen. Table 4 shows that T_i , the soot ignition temperature, is slightly lowered by doping with Zr and increased by the introduction of Y or La, which all increase the rate of soot combustion. In particular, it is difficult to achieve low-temperature soot combustion with the high-temperature bulk oxygen released by $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, although a small reduction peak at 333 °C suggests that a small amount of surface oxygen is available for the activation of soot. A similar variation observed for these three catalysts is that T_m (the temperature at which soot combusts at the highest rate) increases as the major reduction peak temperature increases, without affecting the total H₂ consumption. The lowest T_m and ΔT for soot combustion are obtained using $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_2$, thus revealing that increased participation of lattice oxygen released at lower temperature in soot oxidation

may accelerate the combustion rate. Recently, it has been reported that the incorporation of foreign cations (Zr^{4+} , La^{3+}) into CeO₂ to form Ce-based solid solutions greatly improved the redox properties of CeO₂ as well as its bulk oxygen mobility [25–28]. Therefore, doping of ceria with structure promoter metal cations, which are well known to improve thermal stability and generate lattice defects, does not have a direct favorable effect on the soot ignition temperature because only a small amount of surface oxygen is provided at a low temperature.

Recently, much attention has been paid to CeO₂ modified with alkali and alkaline earth metals because of their low melting points [29–31]. The TPR profiles of 10%A-CeO₂ presented in Fig. 7(b) show reduction peaks that shift to a lower temperature upon modification with Na and K, which indicates a higher availability of surface oxygen because of their excellent flowability. In contrast, introduction of Mg and Ba caused reduction peaks to shift to a higher temperature with larger peak areas, implying that the activation of O₂ is promoted by modification with all alkali and alkaline earth metals. According to the data for 10%A-CeO₂ reported in Table 4, the values of T_m or ΔT , which show little difference in the catalytic activity for soot combustion, are not associated with the total H₂ consumption of each catalyst. That is to say, for 10%A-CeO₂, it can be considered that catalytic activity for soot combustion is not directly affected by the change of reducibility, which only accelerates the overall rate of soot oxidation (with a smaller value of ΔT). In summary, a high rate of soot oxidation is achieved by modification of CeO₂ with alkali and alkaline earth metals, which can increase soot-catalyst contact using low melting points rather than improve redox properties.

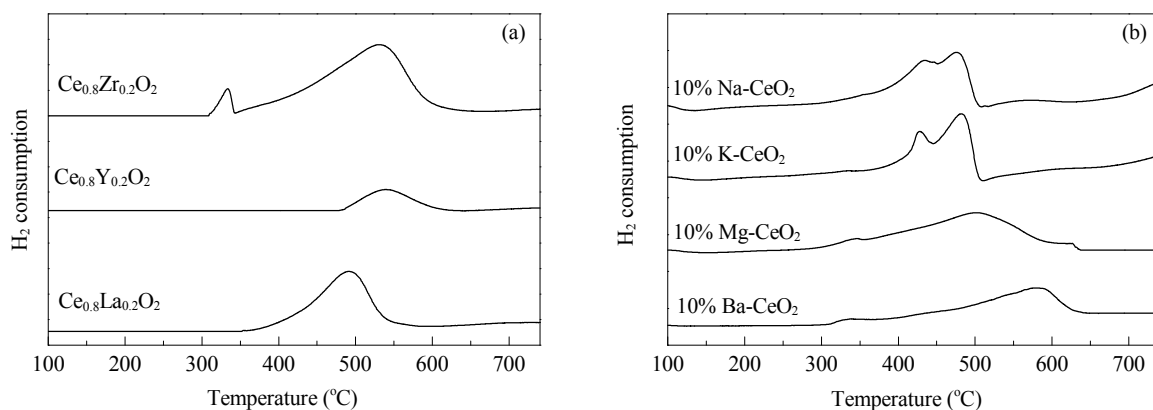


Fig. 7. H₂-TPR profiles of Ce-based catalysts doped with different structure promoter, alkali and alkaline earth metals. (a) $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_2$ (R = Zr, Y, La); (b) 10%A-CeO₂ (A = Na, K, Mg, Ba).

Table 4TPR characterization and catalytic performance for soot combustion by Ce_{0.8}R_{0.2}O₂ and 10%A-CeO₂ catalysts.

Sample	Peak 1		Peak 2		T _i /°C	T _m /°C	T _f /°C
	T/°C	n(H ₂)/(mmol/g)	T/°C	n(H ₂)/(mmol/g)			
Ce _{0.8} Zr _{0.2} O ₂	333	0.070	530	1.335	390	458	502
Ce _{0.8} Y _{0.2} O ₂	538	0.215	—	—	417	474	519
Ce _{0.8} La _{0.2} O ₂	484	0.760	—	—	398	447	484
10%Na-CeO ₂	436	0.550	466	0.270	391	440	467
10%K-CeO ₂	426	0.440	470	0.305	395	452	500
10%Mg-CeO ₂	496	1.345	—	—	393	442	479
10%Ba-CeO ₂	578	1.055	—	—	394	446	488

4. Conclusions

The incorporation of transition metals (Cr, Mn, Fe, Co, Ni, and Cu) into CeO₂ can greatly enhance its low-temperature redox properties, resulting in high catalytic activity for soot oxidation. In particular, the amount of active oxygen released at 200–400 °C plays an important role in improving combustion performance. Doping CeO₂ with structure promoter metals will mainly improve its moderate-temperature redox properties, which leads to a higher combustion rate without affecting soot ignition temperature. Modification of CeO₂ with alkali and alkaline earth metals can improve its ability to catalyze soot oxidation because the low melting points of the resulting materials improve the contact between soot and catalyst, rather than by changing the redox properties of CeO₂.

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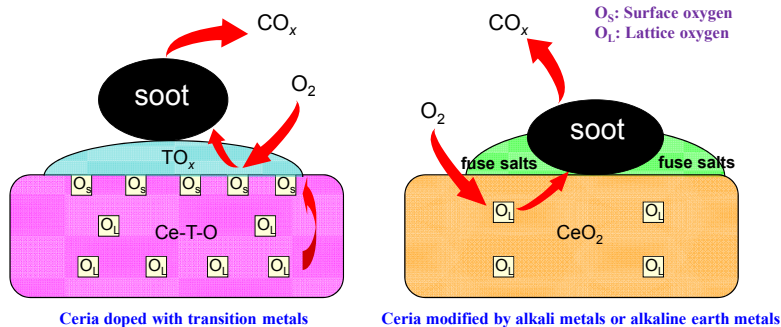
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Graphical Abstract

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Soot combustion performance and H₂-TPR study on ceria-based mixed oxides

SHENG Yeqin, ZHOU Ying, LU Hanfeng*, ZHANG Zekai, CHEN Yinfei
Zhejiang University of Technology



The influence of doping ceria with different kinds of metal ions on its redox properties for soot combustion was investigated. The oxidation temperature of soot could be significantly reduced using ceria doped with transition metals because more active oxygen was generated at low temperature. In contrast, doping ceria with alkali metal and alkaline earth metals increased the combustion rate of soot.

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