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Article

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

ARTICLE INFO

Article history:

Received 22 September 2012

Accepted 5 December 2012

Published 20 March 2013

Keywords:

Soot

Ceria-based mixed oxide

Catalytic combustion

Redox property

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

This work was supported by the National Natural Science Foundation of China (21107096) and the Department of Education of Zhejiang (Y201121401).

DOI: 10.1016/S1872-2067(11)60495-6 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 3, March 2013

cies and amount of active oxygen, particularly the mobility of lattice oxygen, can be analyzed qualitatively and quantitatively by H_2 -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, CeO_2 was doped with transition, structure promoter, alkali and alkaline earth metals and the redox properties of the resulting materials were characterized by H_2 -TPR. The purpose of this work is to gain further insight into the influence of the distribution of active oxygen in CeO_2 -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.

CeO_2 doped with transition metals were formed by the following process. $Cr(NO_3)_3 \cdot 9H_2O$, $Mn(NO_3)_2$, $Fe(NO_3)_3 \cdot 9H_2O$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, or $Cu(NO_3)_2 \cdot 3H_2O$ was dissolved in a solution of $Ce(NO_3)_3 \cdot 6H_2O$ 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 $Ce_{0.8}T_{0.2}O_2$).

CeO_2 doped with structure promoter metals were formed by the following process. $Ce(NO_3)_3 \cdot 6H_2O$ and $Zr(NO_3)_4 \cdot 3H_2O$, $Y(NO_3)_3 \cdot 6H_2O$, or $La(NO_3)_3 \cdot 6H_2O$ were mixed to form solutions with a molar ratio of 0.8:0.2. The resulting catalysts are labeled as $Ce_{0.8}R_{0.2}O_2$.

Loading of alkali or alkaline earth metals on CeO_2 : These catalysts are designated 10%A- CeO_2 (A = Na, K, Mg, Ba) and contain a molar ratio of A/Ce of 10%.

MnO_x - CeO_2 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 $Ce_{1-x}Mn_xO_2$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0$).

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% O_2 -90% N_2 (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_b , 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 $Cu K\alpha$ radiation and were recorded at 0.02° intervals in the range of $10^\circ \leq 2\theta \leq 80^\circ$ at a voltage of 45 kV and current of 30 mA.

The specific surface areas of samples were determined from N_2 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.

H_2 -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% H_2 -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 H_2 was monitored by a thermal conductivity detector (TCD) operating at 60 °C and 60 mA.

3. Results and discussion

3.1. CeO_2 doped with transition metals

3.1.1. Texture of catalysts

Powder XRD patterns of CeO_2 doped with different transition metals are shown in Fig. 1(a). The lattice constants and mean crystallite sizes of CeO_2 in the samples were calculated by Bragg law and Scherrer equation, respectively (Table 1). In the samples, CeO_2 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 CeO_2 . 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 $Ce_{0.8}Cu_{0.2}O_2$ and $Ce_{0.8}Co_{0.2}O_2$ catalysts than that of CeO_2 further confirm that Co and Cu are mainly dispersed on the surface of CeO_2 without forming ceria-based solid solutions. Two diffraction peaks attributed to CuO observed in the XRD pattern of $Ce_{0.8}Cu_{0.2}O_2$ suggest the presence of large CuO_x particles, which is consistent with related literature [11–14]. CeO_2 catalysts doped with Cr, Mn, Fe, and Ni only show the diffraction peaks of CeO_2 , which are all shifted slightly to a higher diffraction angle, especially for the $Ce_{0.8}Mn_{0.2}O_2$ catalyst. This indicates that ceria-based solid solutions are formed by partial replacement of Ce^{4+} with these smaller transition metal cations, decreasing the lattice constant of CeO_2 (Table 1). Doping CeO_2 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 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$ with a shoulder at 150 $^{\circ}\text{C}$, 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 ($T_i = 383$ $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$, 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 $^{\circ}\text{C}$ 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	$2\theta/(^{\circ})$	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)				<i>T</i> _i /°C	<i>T</i> _m /°C	<i>T</i> _f /°C
	Peak 1		Peak 2				
	<i>T</i> /°C	<i>n</i> (H ₂)/(mmol/g)	<i>T</i> /°C	<i>n</i> (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 $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ catalysts.

oxygen released by the samples between 200 and 400 °C because ΔT increased gradually as the amount of H_2 consumed decreased. As stated above, the combination of Co, Cu, and CeO_2 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 $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ catalysts (Fig. 4), which are reported as the transition metal-doped CeO_2 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 $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ 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 $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ is presented in Fig. 2(b). The two reduction peaks of $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ 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 H_2 consumption at 200–400 °C and T_m for $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ catalysts.

dicates that an increase in Mn doping levels leads to a decrease in H_2 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 $\text{Ce}_{0.8}\text{Mn}_{0.2}\text{O}_2$ 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. CeO_2 catalysts of modified by structure promoter, alkali and alkaline earth metals

3.2.1. Texture of catalysts

Powder XRD patterns of $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_2$ and 10%A- CeO_2 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 Ce^{4+} with different structure promoter, alkali and alkaline earth metal cations. XRD peaks shift to lower angles for $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_2$ and higher ones for $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ and $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$, reflecting the order of their ionic radii of $\text{La}^{3+} > \text{Ce}^{4+} > \text{Y}^{3+} > \text{Zr}^{4+}$. In addition, the surface area is significantly increased by doping with Zr but decreased for $\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$ and $\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_2$ 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) $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_2$ ($\text{R} = \text{Zr}, \text{Y}, \text{La}$); (b) 10%A- CeO_2 ($\text{A} = \text{Na}, \text{K}, \text{Mg}, \text{Ba}$).

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

Sample	Peak 1		Peak 2		$T_i/^\circ\text{C}$	$T_m/^\circ\text{C}$	$T_f/^\circ\text{C}$
	$T/^\circ\text{C}$	$n(\text{H}_2)/(\text{mmol/g})$	$T/^\circ\text{C}$	$n(\text{H}_2)/(\text{mmol/g})$			
$\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$	333	0.070	530	1.335	390	458	502
$\text{Ce}_{0.8}\text{Y}_{0.2}\text{O}_2$	538	0.215	—	—	417	474	519
$\text{Ce}_{0.8}\text{La}_{0.2}\text{O}_2$	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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Graphical Abstract

Chin. J. Catal., 2013, 34: 567–577 doi: 10.1016/S1872-2067(11)60495-6

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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铈基复合氧化物催化碳烟燃烧的性能及其H₂-TPR研究

盛叶琴, 周 瑛, 卢晗锋*, 张泽凯, 陈银飞

浙江工业大学催化反应工程研究所, 化学工程与材料学院, 浙江杭州310014

摘要: 采用溶胶-凝胶法或浸渍法制备了不同金属离子掺杂的铈基复合氧化物催化剂, 并采用热重法考察其催化碳烟燃烧的活性, 借助H₂-TPR (程序升温还原) 手段探讨了催化剂氧化还原性对碳烟燃烧性能的影响. 结果表明, 过渡金属的掺杂促使催化剂在低温下提供更多的表面氧和晶格氧, 显著降低了碳烟的氧化温度, 催化剂于200~400 °C释放的活性氧数量对于碳烟燃烧性能提高至关重要; 而结构性助剂金属、碱金属或碱土金属的掺入可提高中温活性氧数量, 虽然对碳烟起燃温度无明显改善, 但加快了碳烟的燃烧速率.

关键词: 碳烟; 铈基复合氧化物; 催化燃烧; 氧化还原性

收稿日期: 2012-09-22. 接受日期: 2012-12-05. 出版日期: 2013-03-20.

*通讯联系人. 电话/传真: (0571)88320767; 电子信箱: luhf@zjut.edu.cn

基金来源: 国家自然科学基金(21107096); 浙江省教育厅(Y201121401).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).

1. 前言

汽车柴油机排放的颗粒物(PM)对人类健康和大气环境都造成了严重的危害^[1], 减少PM的排放已成为一项刻不容缓的任务. 碳烟是PM的主要成分, 在不改变发动机系统和燃料结构的前提下, 催化燃烧技术是目前最直接有效的碳烟后处理方式^[2].

作为碳烟燃烧的基本催化材料, CeO₂因具有良好的储氧能力(OSC)和优异的氧化还原性能而广为报道^[3]. 然而, 单一CeO₂催化碳烟燃烧的活性窗口仍远高于柴油机的尾气温度(< 400 °C), 且高温焙烧会造成CeO₂严重烧结, 从而导致碳烟氧化活性急剧下降. 近年来, 人们通过掺杂过渡金属、稀土金属以及碱金属等, 并与其形成铈基固溶体成为一条简便且能有效提高CeO₂催化性能和热稳定性的途径^[4–8]. 然而, 不同金属离子的掺杂必然会引起CeO₂结构和物理化学特性, 尤其是氧化还原性能的变化. 一般而言, 氧化还原反应遵循 Mars-Van Krevelen 反应机理, 即在碳烟与催化剂保持良好接触的

条件下, 碳烟的氧化是通过金属氧化物的氧化还原循环来实现的^[9]. 许多文献报道也证明, 对于碳烟的催化氧化, 催化剂的活性在很大程度上取决于其能否在一个适宜的低温范围内将活性氧传递到碳烟, 即其氧化还原性是决定活性的关键因素^[6,10].

TPR过程中不仅有高价态金属阳离子被H₂还原成低价态或金属单质, 更涉及晶格氧与H₂反应生成H₂O的过程. 因此, 通过研究铈基氧化物催化剂的TPR过程, 可以定性和定量地分析催化剂中活性氧的种类、数量, 特别是晶格氧移动性的相关信息, 对于催化剂氧化碳烟活性的研究具有深刻的指导意义. 本文制备了不同过渡金属、结构性助剂金属、碱金属或碱土金属掺杂的铈基复合氧化物催化剂, 采用H₂-TPR表征手段探讨了不同催化剂上活性氧分布对碳烟燃烧性能造成的影响及其原因.

2. 实验部分

2.1. 催化剂的制备

采用溶胶-凝胶法制备过渡金属、结构性助剂金属

掺杂的铈基催化剂, 浸渍法制备碱金属或碱土金属掺杂的铈基催化剂, 所掺杂金属的前驱体均为相应的硝酸盐。

(a) 掺杂过渡金属: 以Cr, Mn, Fe, Co, Ni, Cu的硝酸盐和硝酸铈为原料, 体系中铈离子与过渡金属离子的摩尔比为0.8:0.2, 溶于一定量的去离子水后, 加入金属阳离子摩尔量2倍的柠檬酸和柠檬酸质量10%的聚乙二醇, 搅拌蒸干得到凝胶, 于110 °C干燥12 h, 300 °C预烧1 h, 500 °C焙烧3 h, 得到的催化剂记为 $\text{Ce}_{0.8}\text{T}_{0.2}\text{O}_2$ 。

(b) 掺杂Zr, Y和La等结构性助剂金属, 其中铈离子与金属离子的摩尔比为0.8:0.2, 记为 $\text{Ce}_{0.8}\text{R}_{0.2}\text{O}_2$ 。

(c) 负载Na, K, Mg, Ba等碱金属或碱土金属, 其中金属离子占铈离子摩尔量的10%, 记为10%A- CeO_2 。

同时, 采用溶胶-凝胶法制备了不同 $n(\text{Mn})/n(\text{Ce})$ 比的锰铈复合氧化物, 于500 °C焙烧3 h, 得到的催化剂记为 $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ ($x = 0.2, 0.4, 0.6, 0.8, 1.0$)。

2.2. 催化剂的活性评价

采用热重(TG)分析仪(德国Netzsch STA 409PC)对催化剂活性进行测试。将碳烟(德国Degussa公司生产的Printex-U商业模拟碳烟)和催化剂按1:10 (质量比)的比例混合, 在玛瑙研钵中仔细研磨10 min后装样(达到紧密接触以研究最佳条件下催化剂的本征活性)。取约10 mg样品置于热平衡反应室, 反应气为10% O_2 -90% N_2 , 流量50 ml/min, 从25程序升温到650 °C, 升温速率10 °C/min。

催化剂的活性评价标准为: (a) 碳烟的起燃温度 T_i (TG曲线的外推起始点); (b) 碳烟燃烧速率最大时的温度 T_m (DTG曲线的峰值点); (c) 碳烟的燃烧终止温度 T_f (TG曲线的外推终止点)。

2.3. 催化剂的表征

X射线粉末衍射(XRD)在ARLS CINTAG X'TRA型X射线衍射仪(Ni滤波, Cu K_α 辐射源)上测定, 管电压为45 kV, 管电流为40 mA, 扫描范围 $2\theta = 10^\circ \sim 80^\circ$, 步长为 $0.02^\circ/\text{s}$ 。

样品的比表面积采用美国麦克公司的ASAP 2020M型全自动表面积及微孔孔隙分析仪测试, 于300 °C抽真空预处理2 h, 以 N_2 为吸附质, -196 °C进行测定。采用BET法计算样品的比表面积。

H_2 -TPR实验在衢州泛泰生产的FINESORB-3010E型化学吸附仪上进行。催化剂装量为0.2 g, CuO作为标样。首先在Ar气氛下200 °C预处理1 h, 冷却至100 °C, 然后通入5% H_2 -95%Ar的还原气, 在100 °C吹扫20 min, 再以10 °C/min升温至750 °C, 最后又用Ar气吹扫降温, 其中载气流速均为30 ml/min。TCD检测器, TCD池温度60

°C, TCD电流60 mA。

3. 结果与讨论

3.1. 过渡金属掺杂的铈基氧化物催化剂

3.1.1. 催化剂的织构性质

图1(a)为不同过渡金属掺杂的铈基氧化物的XRD谱。根据Bragg和Scherrer公式计算所得晶格常数和晶粒尺寸列于表1。可以看出, 纯 CeO_2 检测为立方萤石结构。过渡金属的离子半径均小于铈离子, 但掺杂Cu后 CeO_2 的晶胞参数基本无明显变化; $\text{Ce}_{0.8}\text{Co}_{0.2}\text{O}_2$ 则出现一定的晶格膨胀, 两者比表面积的减小进一步说明Co和Cu主要以氧化物形式分布在 CeO_2 表面, 而Co主要以氧化物微晶形式存在, 大晶粒 CuO_x 则导致出现CuO晶相, 与文献^[11–14]结果一致。Cr, Mn, Fe, Ni等过渡金属掺杂后催化剂上均只检测到 CeO_2 的特征衍射峰, 并向高角度位移, 说明这些金属离子溶入了 CeO_2 晶格, 并引起晶格常数的减小, 形成了良好的固溶体结构, 其中以 $\text{Ce}_{0.8}\text{Mn}_{0.2}\text{O}_2$ 最为明显。过渡金属的掺杂有利于催化剂晶粒尺寸减小, 并提高其比表面积, 如 CeO_2 掺杂为 $\text{Ce}_{0.8}\text{Mn}_{0.2}\text{O}_2$, 其晶粒尺寸由11.7 nm减小为7.8 nm, A_{BET} 由29.7增至77.4 m^2/g 。

另外, 较多的文献认为, Mn-Ce固溶体结构更有利于碳烟的催化氧化^[4,12,14]; 为此对Mn-Ce固溶体中Mn的掺杂量进行了考察。如图1(b)所示, 随着Mn摩尔分数(x)的增加, $\text{Ce}_{1-x}\text{Mn}_x\text{O}_2$ 催化剂由单一的 CeO_2 衍射峰逐渐向 MnO_x 转变且峰形变得尖锐, 催化剂的晶粒尺寸与Mn摩尔分数成正比(见表1)。Kang等^[15]研究发现, 掺入Mn-Ce固溶体的锰离子量在很大程度上取决于催化剂的制备方法, 其溶度限制在5%~10%, 多余的Mn则主要以 MnO_x 形式分散于催化剂表面。因此当 $x = 0.2$ 和 0.4 时, 虽只检测到 CeO_2 的特征衍射峰, 但仍有少量小颗粒 MnO_x 物种高度分散于表面。而随着Mn含量的进一步提高, Mn-Ce固溶体在整个催化剂中的比例下降, 大量 MnO_x 颗粒的聚积导致晶粒尺寸的增大和比表面积的减小, 故 $\text{Ce}_{0.4}\text{Mn}_{0.6}\text{O}_2$ 和 $\text{Ce}_{0.2}\text{Mn}_{0.8}\text{O}_2$ 出现明显的 MnO_x 衍射峰。

3.1.2. H_2 -TPR表征及碳烟燃烧性能

图2为各过渡金属掺杂的铈基催化剂的TPR谱, 由图2(a)可见, 纯 CeO_2 只在453 °C出现一个还原峰, 归属于 $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ 的还原。掺入过渡金属后, 所有复合氧化物的还原峰均向低温方向移动且峰面积增大, 说明其低温氧化还原性明显提高; Co, Cu与Ce基本上未形成固溶体结构, 但其复合氧化物同样表现出优异的低温氧化还原性, 特别是 $\text{Ce}_{0.8}\text{Cu}_{0.2}\text{O}_2$ 样品在196 °C就出现一个主还原

峰并伴随150 °C的肩峰。研究表明, CuO中添加CeO₂后能明显提高催化剂的OSC, 使其还原峰迅速向低温位置移动且峰形变窄^[16]; 但Ce_{0.8}Cu_{0.2}O₂催化碳烟的起燃温度相比于其他过渡金属为最高($T_i = 383$ °C, 见表2)。由于碳烟的氧化需要提供相当高的活化能才能进行^[17], 而目前包括贵金属催化剂也无法将碳烟起燃温度降到200 °C以下, 因此Ce_{0.8}Cu_{0.2}O₂在200 °C前提供的表面氧应该不足以活化石烟。研究证实, Co-Ce复合氧化物中的Co主要以Co₃O₄形式存在^[18]; 而Ce_{0.8}Co_{0.2}O₂的还原峰(319 °C)低于Co₃O₄的(350~400 °C)^[19], 且对于碳烟氧化具有良好的催化活性, 说明Co₃O₄微晶与CeO₂的协同作用显著增强了催化剂的低温供氧能力。

过渡金属Cr, Mn, Fe, Ni掺入CeO₂晶格后形成了固溶体结构, 有利于进一步提高催化剂的OSC, 其氧化还原性在一定程度上对碳烟燃烧性能造成了规律性的影响。比如Cr掺入后346 °C处的还原峰说明其提供的少量表面氧使碳烟的 T_i 从397 °C降至375 °C, 但中高温段体相氧数量较少导致碳烟燃烧速率降低, 表现为 $\Delta T = T_f - T_i$ (碳烟起燃温度与燃尽温度之间的差值)变大。铁铈氧化物的两个还原峰一般认为是Fe₂O₃→Fe₃O₄和Fe₃O₄→FeO的转变^[20], 第一个还原峰峰温(360 °C)恰好是碳烟的起燃温度, 而大量高温段晶格氧无法及时补给碳烟低温燃烧所需, 致使其在502 °C才燃烧完全。比较各催化剂还原峰位置, 只有Ce_{0.8}Mn_{0.2}O₂几乎都落在能够活化石烟燃烧的温度范围内, 出现分别归属于Mn₂O₃→Mn₃O₄和Mn₃O₄→MnO的两个还原峰^[21], 第一个尖锐的还原峰说明该温度范围内表面氧的迁移速率较快, 促使碳烟在347 °C起燃。Ce_{0.8}Mn_{0.2}O₂表现出最佳的碳烟低温催化活性, 与其低温范围内高密度、高移动性的活性氧物种密切相关。

柴油机的正常尾气温度一般在200~400 °C^[22]。因此, 催化剂在该温度段的活性氧释放能力是决定碳烟燃烧活性的重要因素。对图2(a)中TPR曲线在200~400 °C的还原峰面积进行积分, 由CuO标样计算得到单位质量催化剂的耗氢量如图3所示。可以看出, 碳烟氧化的 ΔT 值随催化剂在200~400 °C的耗氢量的减小而逐渐增大, 即碳烟的燃烧速率与催化剂在200~400 °C内释放的活性氧数量呈现良好的正相关。因此, 就紧密接触条件下过渡金属-铈基氧化物催化碳烟燃烧的过程而言, Co, Cu与CeO₂的结合主要促进表面氧的形成, 而Cr, Mn, Fe或Ni掺入后形成的固溶体结构更有利于晶格氧的释放, 低温(主要是200~400 °C)下丰富的两部分活性氧的协同作用

是保证催化剂优良催化活性的关键。

作为低温催化活性最高的过渡金属-铈基氧化物催化剂, Ce_{1-x}Mn_xO₂的晶粒尺寸与比表面积的变化规律正好相反(见图4), 即紧密接触下Ce_{1-x}Mn_xO₂催化剂的低温活性(见表2)与其晶粒尺寸成反比, 而随其比表面积的增加而逐渐升高。通过改变催化剂与碳烟的接触机会和供氧能力, 晶粒尺寸和比表面积在一定范围内成为影响Ce_{1-x}Mn_xO₂催化活性的重要因素。图2(b)考察了Mn掺杂量对Ce_{1-x}Mn_xO₂氧化还原性的影响。由图可见, 随着 x 的增大, 各锰铈氧化物在450 °C前出现的2个还原峰均依次向高温方向移动, 第一个还原峰峰形逐渐平缓且峰面积呈减小趋势, 第二个还原峰与之恰好相反。催化剂在200~400 °C的耗氢量亦随Mn掺杂量的增加而逐渐减少, 而其氧化碳烟速率最快时的温度 T_m 逐渐降低(见图5)。因此, Ce_{0.8}Mn_{0.2}O₂催化剂优异的低温活性来源于其较小的晶粒尺寸、较大的比表面积, 尤其是催化剂在200~400 °C的持续供氧能力。

3.2. 结构性助剂金属、碱金属或碱土金属掺杂的铈基氧化物催化剂

3.2.1. 催化剂的织构性质

图6给出了Ce_{0.8}R_{0.2}O₂和10% A-CeO₂催化剂的XRD谱; 表3为它们的结构性质。由表可见, 样品晶格常数的变化证实结构性助剂金属、碱金属或碱土金属离子均部分掺杂进入CeO₂晶格形成了固溶体结构。由于离子半径La > Ce > Y > Zr, 因而Ce_{0.8}La_{0.2}O₂的衍射峰向左偏移, Ce_{0.8}Zr_{0.2}O₂和Ce_{0.8}Y_{0.2}O₂与此相反。Zr的掺入显著提高了催化剂的比表面积, 但因进入CeO₂晶格的Y和La离子较少, 其金属氧化物在CeO₂表面分散, 使Ce_{0.8}Y_{0.2}O₂和Ce_{0.8}La_{0.2}O₂的比表面积有所下降。碱金属或碱土金属的掺入同样使催化剂的晶粒尺寸减小, 而对比表面积的影响有所不同: 一价Na⁺或K⁺的添加提高了催化剂的比表面积, 其原因可能是由于Na⁺, K⁺的表面流动性更强^[23]; 而掺杂二价Mg²⁺或Ba²⁺后易于在表面形成碳酸盐物种, 如在10% Ba-CeO₂上可检测到明显的BaCO₃晶相, 碳酸盐覆盖在固溶体表面使其比表面积降低^[24]。

3.2.2. H₂-TPR表征及碳烟燃烧性能

图7(a)为Ce_{0.8}R_{0.2}O₂催化剂的TPR谱。与CeO₂相比, 结构性助剂金属的掺入使其还原峰向高温方向移动, 而峰面积明显增大, 说明催化剂中高温段的晶格氧增加。由表4可知, 只有Zr掺入后使催化剂的起燃温度 T_i 有所下降, 而Y和La的加入反而使 T_i 滞后, 但都在一定程度上提高了碳烟的燃烧速率。Ce_{0.8}Zr_{0.2}O₂在333 °C处出现一小

面积还原峰,说明少量表面氧对活化碳烟氧化起到了一定作用,而中高温段释放的体相氧不足以满足碳烟低温燃烧所需.各催化剂的 T_m (催化碳烟燃烧速率最大时的温度)主要随催化剂主还原峰温度的升高而升高,而基本不受总耗氢量的影响.由于 $Ce_{0.8}La_{0.2}O_2$ 能在较低温度下释放晶格氧加速碳烟的燃烧,因而具有最低的 T_m 和 ΔT 值.研究表明,掺入的Zr,La等通过与 CeO_2 形成良好的固溶体结构,不仅改善了催化剂的氧化还原性,而且增加了体相氧的流动性^[25~28].因此,我们认为,结构性助剂金属的主要作用是增强 CeO_2 的热稳定性和形成更多晶格缺陷易于体相氧的活动,而由于其低温表面氧数量较少,对于碳烟的起燃温度并无实质的影响.

碱金属或碱土金属修饰的铈基复合氧化物因其低熔点而成为一类备受关注的碳烟燃烧催化剂^[29~31].由图7(b)可知,Na和K的加入使得还原峰向低温偏移,说明其流动性促进了催化剂表面氧的活化;而Mg和Ba的掺入导致还原峰明显向高温移动,而峰面积明显增大.因而碱金属或碱土金属的掺入均在一定程度上对 O_2 有活

化作用.由表4可见,各10%A- CeO_2 催化剂的活性相差不大,其总耗氢量与碳烟氧化的 T_m 或 ΔT 并不关联,即其掺杂后引起的氧化还原性变化并不影响碳烟的燃烧活性,但可使反应速率加快(ΔT 变小).因此,碱金属或碱土金属在碳烟燃烧中的作用主要是利用其低熔点促进碳烟与催化剂的接触来提高碳烟的燃烧效率,而不是通过提高催化剂的氧化还原性.

4. 结论

(1)过渡金属Cr, Mn, Fe, Co, Ni, Cu的掺杂能明显改善 CeO_2 的低温氧化还原性,从而提高了其催化燃烧碳烟能力,特别是它们在200~400 °C释放的活性氧对碳烟的燃烧性能提高至关重要;(2)结构性助剂金属Zr, Y, La的掺入提高了 CeO_2 中温区的氧化还原性,明显加快了碳烟的燃烧速率,但对起燃温度基本无改善;(3)碱金属或碱土金属掺杂引起 CeO_2 氧化还原性的变化并不影响催化剂上燃烧活性,它们只是利用其低熔点的特性改善了碳烟与催化剂的接触,从而提高催化性能.