K/CeO₂催化剂上碳黑催化燃烧性能及稳定性

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摘要: 采用不同的钾盐前体制备了一系列 K/CeO₂ 催化剂, 利用热重和程序升温氧化 (TPO) 等技术考察了其催化性能及稳定性. 结果表明, K/CeO₂ 催化剂可使碳黑完全燃烧温度降低近 200 ℃. 钾盐前体对催化活性和稳定性具有较大影响, 由于硝酸钾熔点低, 金属在载体上的流动性强, 有利于催化剂与碳黑的有效接触, 因而表现了较高的活性, 三次 TPO 循环试验中催化活性稳定. 碳酸钾的熔点高且碱性较强, 使碳黑燃烧生成的 CO₂ 不可逆吸附在其表面, 导致反应活性低, TPO 循环实验表明其反应速率降低, 失活明显.

关键词: 碳黑氧化; 钾; 氧化铈; 程序升温氧化; 稳定性

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Catalytic Activity and Stability of K/CeO₂ Catalysts for Diesel Soot Oxidation

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Abstract: A series of CeO₂ supported potassium nitrate and carbonate catalysts were prepared by an impregnation method. The catalytic activity and stability for soot oxidation were investigated by thermal gravimetric/differential thermal analysis and temperature-programmed oxidation cycle techniques. K/CeO₂ substantially promotes the catalytic activity, which can be gauged by the lowering of the soot total removal temperature by more than 200 ℃ compared with the uncatalyzed reaction. The influence of K precursor on the catalytic activity and stability was addressed. The effect is discussed in terms of the combined functions of K and CeO₂, potassium mobility and basicity. For potassium-promoted ceria catalysts the potassium nitrate can preserve the high catalytic activity and good stability through several cycles. When K was present as K₂CO₃, the activity and stability of catalyst were lower than those of KNO₃/CeO₂. This behavior is attributed to the higher melting point and stronger basicity of K₂CO₃ which lead to irreversible adsorption of CO₂ generated during soot combustion on the catalyst.

Key words: soot oxidation; potassium; ceria; temperature-programmed oxidation; stability

Exhaust gas abatement in diesel engines, especially soot, is now a major challenge for environmental protection [1]. Normally soot can be oxidized without any catalyst by oxygen at around 600 ℃ [2]. However, the exhaust gas temperature is below 300 ℃ during most diesel engine operations, which is too low to initiate continuous

un-catalyzed soot oxidation [3,4]. Therefore, it is crucial to develop more active catalysts for simultaneous soot combustion [5]. The most active catalysts reported in the literature included oxides such as mixed metal oxides [6], noble metals, rare earth metal oxides, and perovskite [7,8]. In which, ceria and ceria-based catalysts have displayed an attractive potential in the field of catalytic removal of soot from diesel engines exhaust gas [9–12]. Ceria/doped ceria has unique properties such as oxygen storage/release capability (OSC) and fast redox (Ce^{3+}/Ce^{4+}) cycle capability [13], which make it possible to provide oxygen species for soot oxidation at low temperature [14]. However, the soot ignition temperature on ceria catalysts is still higher than the exhaust gas temperature of diesel engines. It was reported that K/CeO_2 is an effective system which has potassium as the active site for soot combustion [15,16] and potassium nitrate impregnation increased the stability against sulfur poisoning of soot oxidation catalysts due to preferential sulfatization of potassium [17]. Alkaline metal oxides accelerate the formation of superoxides and peroxides on the surface of cerium oxide, and these species may initiate the soot oxidation [18,19] via the formation of atomic oxygen species (O_{ad}). The potassium compounds can improve the catalytic activity of ceria oxide due to an electron-donating effect, which can increase the local electron density of neighboring carbon sites and promote their affinity for binding an oxygen atom [20]. It has been reasonably established that K improves the catalytic activity due to its high mobility, favoring the contact with soot due to its low melting point [2,17,21,22] and increasing the surface mobility of oxygen species formed on the K compounds. So, many attempts have been made to elaborate catalysts for soot oxidation on the basis of either simple or mixed metal oxides. However, the stability of the catalysts is negligible. The aim of this work was to evaluate the effect of the potassium compound in K/CeO_2 on the catalytic activity and stability in soot oxidation.

1　Experimental

1.1　Preparation of materials

CeO₂ was synthesized by the sol-gel method. The nitrate $Ce(NO_3)_3·6H_2O$ (99.0 wt%, Shanghai) was added into deionized water to give a solution of 1.0 mol/L (50 ml). Then a 1.2 times molar amount of citric acid was added to the solution followed by heating and evaporating to dryness under vigorous stirring, and burning or explosion. Finally the precursor was calcined at 450 ℃ for 3 h in static air.

K/(KNO₃+CeO₂) catalysts with 6 wt%, 11 wt%, 19 wt%, and 26 wt% K loadings and K/(K₂CO₃+CeO₂) catalysts with 7 wt%, 12 wt%, 23 wt% or 33 wt% K loadings were pre-

pared by an impregnation method, respectively. CeO₂ was added into a solution which contained xKNO₃ (99.0 wt%, Tianjin) or xK₂CO₃ (99.0 wt%, Tianjin) to form a suspension (x = 0.1, 0.2, 0.5, and 1 mol/L). The mixture was heated while being vigorously stirred until a paste was obtained, which was dried at 120 ℃ for 24 h in air and calcined at 400 ℃ for 2 h.

1.2　Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Siemens D-5000 powder diffractometer by using nickel-filtered Cu $K_α$ radiation ($λ$ = 0.15406 nm).

1.3　Catalytic activity measurement

The thermal gravimetric analysis (TG-DTA) of catalyst-soot mixture samples was carried out in a Diamond TG/DTA apparatus (Perkin Elmer instruments). The catalytic activity was measured with catalyst–soot mixtures in an 80:20 mass ratio. Printex-U from Degussa S. A. was used as model soot. A sample (having less than 2 mg of soot) was placed in a TGA crucible and heated to 800 ℃ with a rate of 10 ℃/min in a 20 ml/min air flow. The soot conversion between 350 and 600 ℃ was normalized to 1 to eliminate the small differences between soot masses. In this work the soot ignition temperature (denoted as T_{10}), maximum conversion temperature (denoted as T_{50}), complete conversion temperature (denoted as T_{90}), thermal peak temperature (denoted as T_{max}) and temperature window (denoted as $ΔT = T_{90} - T_{10}$) were used to evaluate the performance of the catalysts.

The catalytic stability was evaluated in a home-made temperature-programmed oxidation (TPO) reaction apparatus. The catalyst was mixed with soot in an 80:20 mass ratio producing a loose contact mode which is more comparable to practical applications. The mixture (100 mg) and 250 mg of quartz sand were packed between two quartz wool plugs in a tubular quartz reactor (i.d. = 6 mm), and the oxidation process was carried out at 360 ℃ and lasted over 300 min. The used catalyst was mixed with 20 mg soot to repeat the oxidation process. The inlet gas mixture was 50% air + 50% N₂ with a total flow rate of 100 ml/min. The concentrations of CO₂ and CO in the outlet gases were determined on-line by a GC.

2　Results and discussion

2.1　Influence of K promotion on the catalytic activity for soot oxidation

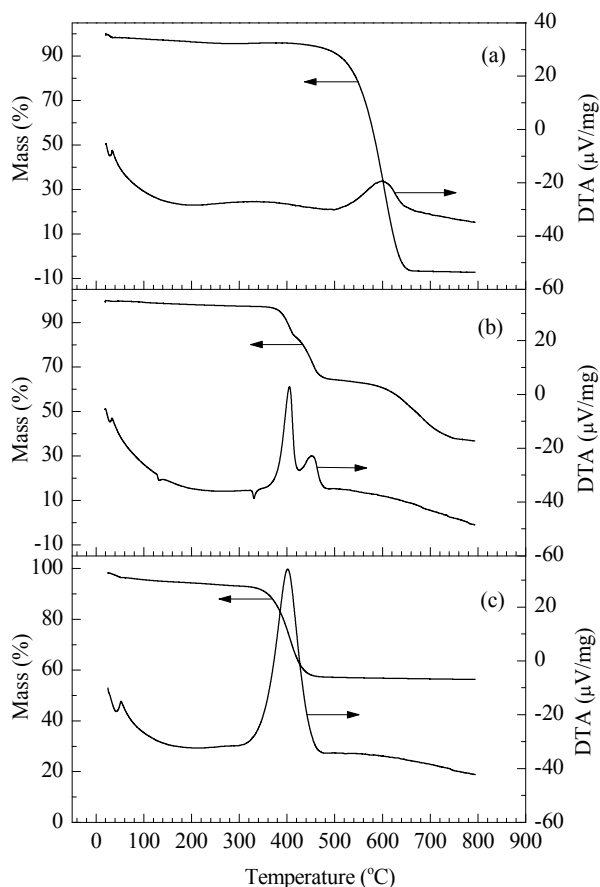Figure 1 shows the TG-DTA curves of uncatalyzed reac-

Fig. 1. TG-DTA curves. (a) C; (b) KNO$_3$ + C; (c) CeO$_2$ + C.

tion (C) and KNO$_3$ (KNO$_3$ + C) and CeO$_2$ (CeO$_2$ + C) as catalyzed reaction. A mass loss of 100 wt% was observed between 500 and 650 ℃ for the free-catalyst according to the TG curve in Fig. 1. The DTA curve exhibited one exothermic peak at 597 ℃ corresponding to the T_{max}. A three stage mass loss was detected in the TG-DTA curve when the soot oxidation occurred over KNO$_3$. The second stage mass loss of ca. 30 wt% between 350 and 450 ℃ was attributed to the loss due to soot combustion. According to the TG results two exothermic peaks were observed in DTA profile of the soot oxidation process. The first peak detected at relatively low temperature corresponds to a fast oxidation process, whereas the second peak corresponds to a slower one [4,23,24]. These phenomena can be explained by soot-catalyst contact and related to heat and oxygen transport limitations. The mass loss of the sample should be around 20 wt% on the TG curve when the catalysts and soot were mixed in a mass ratio of 80:20. However, the mass loss has a deviation of 5 wt% more or less as result of the error produced during weighing and grinding of the sample. Another contribution to the mass loss that should be considered is the decomposition of KNO$_3$ to KNO$_2$ which happened between 350 and 400 ℃. The mass loss above 450 ℃ is attributed to the loss of KNO$_3$ decomposed to K$_2$O. The

TG-DTA curves obtained from soot oxidation in the presence of CeO$_2$ have been also shown in Fig. 1. It shows one mass loss between 300 and 450 ℃. CeO$_2$ showed the fastest soot conversion among the three samples. As shown in Fig. 2 the temperature window ΔT was 70 ℃ over CeO$_2$.
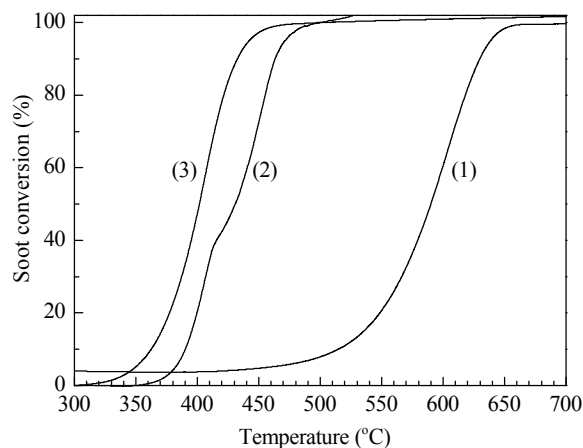

Fig. 2. Soot conversion as a function of temperature. (1) C; (2) KNO$_3$ + C; (3) CeO$_2$ + C.

The characteristic temperatures for soot oxidation are listed in Table 1. The temperature values T_{10}, T_{50}, T_{90}, T_{max}, and ΔT were significantly low when KNO$_3$ or CeO$_2$ was used as catalyst compared with those of the un-catalyzed soot oxidation. T_{max} was 403 and 400 ℃ over KNO$_3$ and CeO$_2$, respectively, decreasing about 190 ℃ as compared with the un-catalyzed reaction (T_{max} = 597 ℃). The effect of the catalyst is also indicated by a narrowing of the temperature window. The value of ΔT was decreased by 18 ℃ as compared with the un-catalyzed reaction (ΔT = 88 ℃). CeO$_2$ showed better soot oxidation activity than KNO$_3$ as indicated by a 30 ℃ decrease in T_{10}, T_{50}, and T_{90} (Table 1).

Figures 3 and 4 display the TG-DTA curves of CeO$_2$ catalysts doped with KNO$_3$ and K$_2$CO$_3$, respectively. A three stage mass loss was observed with the increase of

Table 1 Catalytic activity parameters from TG-DTA for soot oxidation

Sample	Temperature (℃)				
	T_{10}	T_{50}	T_{90}	T_{max}	ΔT
Soot (C)	530	590	630	597	88
KNO$_3$ + C	390	430	460	403	70
CeO$_2$ + C	362	402	433	400	70
6 wt% K/(KNO$_3$+CeO$_2$)	369	397	411	400	42
11 wt% K/(KNO$_3$+CeO$_2$)	367	392	403	396	36
19 wt% K/(KNO$_3$+CeO$_2$)	374	397	407	400	33
26 wt% K/(KNO$_3$+CeO$_2$)	378	403	417	394	39
7 wt% K/(K$_2$CO$_3$+CeO$_2$)	367	369	418	400	51
12 wt% K/(K$_2$CO$_3$+CeO$_2$)	360	390	413	390	53
23 wt% K/(K$_2$CO$_3$+CeO$_2$)	357	386	407	390	50
33 wt% K/(K$_2$CO$_3$+CeO$_2$)	359	387	410	390	51
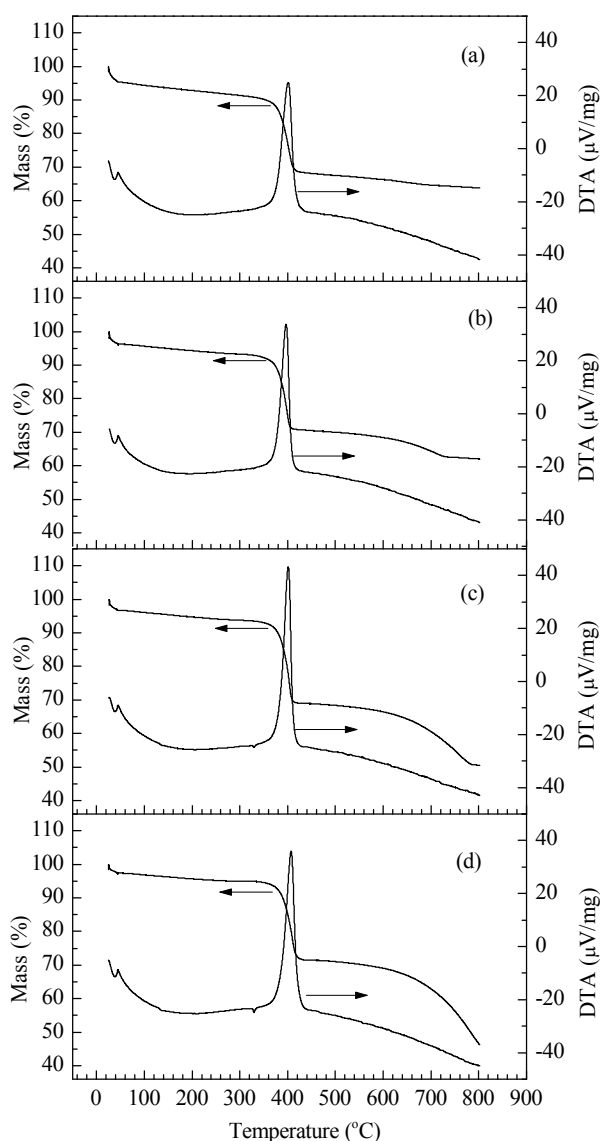
Fig. 3. TG-DTA curves for CeO$_2$ catalysts doped with KNO$_3$. (a) 6 wt% K/(KNO$_3$ + CeO$_2$); (b) 11 wt% K/(KNO$_3$ + CeO$_2$); (c) 19 wt% K/(KNO$_3$ + CeO$_2$); (d) 26 wt% K/(KNO$_3$ + CeO$_2$).

Fig. 4. TG-DTA curves for CeO$_2$ catalysts doped with K$_2$CO$_3$ (a) 7 wt% K/(K$_2$CO$_3$+CeO$_2$); (b) 12 wt% K/(K$_2$CO$_3$+CeO$_2$); (c) 23 wt% K/(K$_2$CO$_3$+CeO$_2$); (d) 33 wt% K/(K$_2$CO$_3$+CeO$_2$).

KNO$_3$ (Fig. 3). The about 22 wt% mass loss between 300 and 400 ℃ was attributed to the loss due to soot combustion and the decomposition of KNO$_3$ to KNO$_2$ which happened between 350 and 400 ℃. The mass loss above 400 ℃ increased with potassium content (from 5 wt% to 26 wt%) and was attributed to the loss of KNO$_3$ decomposing to K$_2$O according to the following equations: KNO$_3$ = KNO$_2$ + 1/2 O$_2$ and 2KNO$_2$ = K$_2$O + NO + NO$_2$. As shown in Table 2 the mass loss in the experiment was lower than the calculated theoretical value. It indicated that KNO$_3$ had not completely decomposed. Figure 4 shows the two stage mass loss over K/(K$_2$CO$_3$+CeO$_2$) for soot oxidation. The first stage below 400 ℃ with a mass loss of about 19 wt% is attributed to soot combustion. As potassium content was increased, the
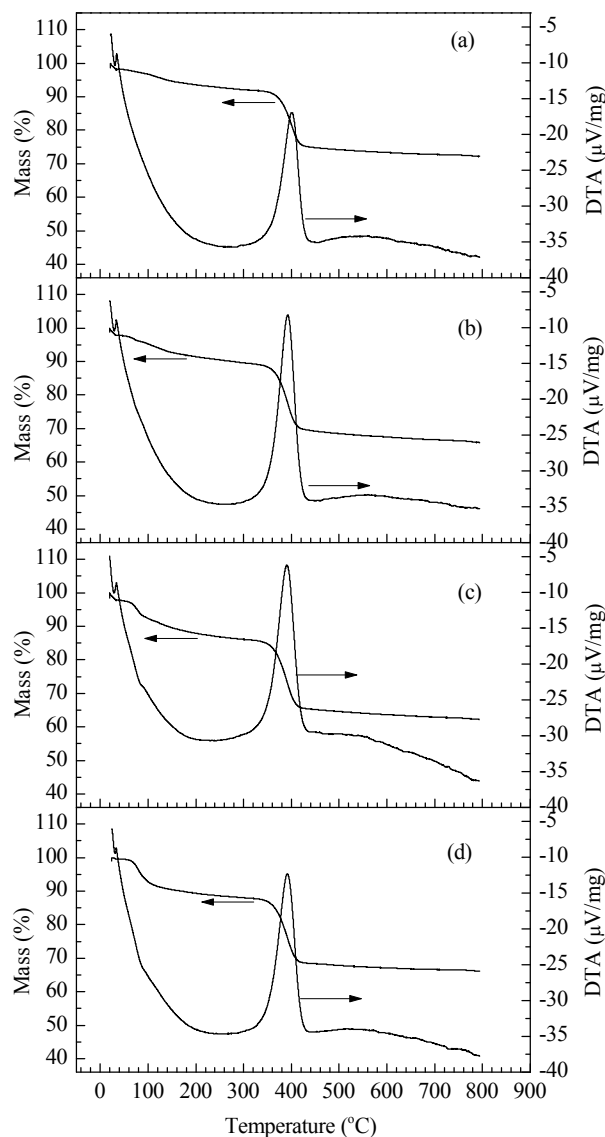
mass loss at high temperature was very similar (i.e. 4 wt% to 5 wt%) which is very different from the case of K/(KNO$_3$+CeO$_2$).

The influence of K compound on soot oxidation is compared in Table 1. From Table 1 it can be seen that the addition of K improved the catalytic activity for soot oxidation and the characteristic temperatures including T_{50}, T_{90}, and ΔT were significantly lower over K/(KNO$_3$+CeO$_2$) than those over CeO$_2$ or KNO$_3$. A further narrowing of ΔT was obtained to 33–42 ℃ for K/(KNO$_3$+CeO$_2$) and 50–53 ℃ for K/(K$_2$CO$_3$+CeO$_2$), respectively. These results suggest that K and CeO$_2$ are a good combination to oxidize the soot particles and lead to the most active catalyst. Krishna et al. [25] reported that the activation of oxygen and spill over of ac-

Table 2 The mass loss from TG-DTA experiments and calculated theoretical results

Sample	Mass loss at low temperature (mg)		Mass loss at high temperature (mg)	
	Calculation[a]	Experiment	Calculation[b]	Experiment
6 wt% K/(KNO$_3$+CeO$_2$)	20	23	7.1	5
11 wt% K/(KNO$_3$+CeO$_2$)	20	22	12.2	9
19 wt% K/(KNO$_3$+CeO$_2$)	20	22	21.4	18
26 wt% K/(KNO$_3$+CeO$_2$)	20	21	28.5	26
7 wt% K/(K$_2$CO$_3$+CeO$_2$)	20	17	—	—
12 wt% K/(K$_2$CO$_3$+CeO$_2$)	20	18	—	—
23 wt% K/(K$_2$CO$_3$+CeO$_2$)	20	19	—	—
33 wt% K/(K$_2$CO$_3$+CeO$_2$)	20	19	—	—

All the calculations are based on 100 mg sample.

[a] Only soot oxidation was considered.

[b] Calculation according to $2KNO_3 = K_2O + NO + NO_2 + O_2$.

tive oxygen from gas to soot particles are important intermediate steps in the soot oxidation over the catalyst. Several authors pointed out the importance of the redox properties of the catalyst, that is, the effectiveness of the catalyst can be related to its ability to deliver oxygen from the lattice to the gas phase. Ceria and doped ceria have unique properties such as oxygen storage and release capability (OSC) and fast redox cycle capability due to their ability to change oxidation state (Ce^{3+}/Ce^{4+}) during operation while maintaining structural integrity [11], which make it possible to provide oxygen species for soot oxidation at low temperature [12]. The doped K accelerated the adsorption of oxygen and promoted the formation of active oxygen in the reaction [26].

Table 1 shows the activity results for the catalysts prepared with different K precursors. The K/(KNO$_3$+CeO$_2$) catalysts exhibited higher activity than the K/(K$_2$CO$_3$+CeO$_2$) catalysts. It is known that the catalytic activity for soot oxidation correlates with the Tamman temperature of the compounds present on the catalytic surface. This characteristic temperature corresponds to approximately half of the melting point and is related to the mobility of the species on the catalytic surface [20,27]. The lower the value of the Tamman temperature, the higher the compound mobility on the surface, thus increasing the probability of contact between the catalyst and the soot particles and consequently increasing the catalytic activity. The melting points of KNO$_3$ and K$_2$CO$_3$ are 333 and 891 ℃, respectively. The low melting point of potassium nitrate played a key role in enhancing the activity for this reaction. The NO$_x$ produced from the decomposition of KNO$_3$ promoted soot oxidation as well because soot oxidation occurs at lower temperatures in the presence of NO$_x$ [28].

2.2 Catalytic stability at low temperatures

The catalytic stability was studied by carrying out TPO experiments with three cycles. Soot (about 20 mg) was added before each new cycle. The results are shown in Fig. 5. In each TPO cycle a higher CO$_2$ and CO concentration reach a maximum in shorter time over the 19 wt% K/(KNO$_3$+CeO$_2$) catalyst compared with the previous cycle. This indicates that this catalyst maintained a good reaction rate after several cycles, i.e., 19 wt% K/(KNO$_3$+CeO$_2$) catalyst showed a good stability through the three TPO cycles. Figure 5(b) shows the results through three TPO cycles over the 23 wt% K/(K$_2$CO$_3$+CeO$_2$) catalyst. They are very different from the 19 wt% K/(KNO$_3$+CeO$_2$) catalyst. The TPO profiles obtained with the catalyst prepared using KNO$_3$ display one sharp peak while the TPO profiles obtained with catalysts prepared using K$_2$CO$_3$ display one small and broad peak. This is due to the higher basicity of these catalysts which leads to a stronger interaction with
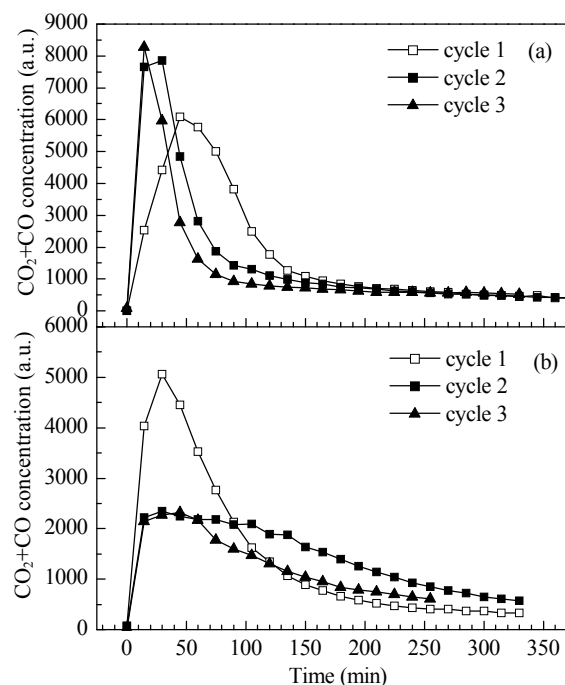

Fig. 5. TPO profiles of soot oxidation over 19 wt% K/(KNO$_3$+CeO$_2$) (a) and 23 wt% K/(K$_2$CO$_3$+CeO$_2$) (b) catalysts.

CO_2 during the soot combustion reaction so that a longer time was needed to oxidize the soot completely. The soot oxidation rate decreased after every cycle over 23 wt% $K/(K_2CO_3+CeO_2)$. The maximum value of CO_2 + CO concentration was about 0.5% in the first cycle, but it was only half of that in the second and third cycle. In short, the potassium nitrate can maintain the high catalytic activity and good stability of potassium-promoted ceria catalysts through several cycles and even improve the catalytic performance further, whereas the performance of the potassium carbonate catalyst became worse.

In order to clarify the difference in stability during soot oxidation between 19 wt% $K/(KNO_3+CeO_2)$ and 23 wt% $K/(K_2CO_3+CeO_2)$, XRD analysis was carried out to study the structure change of catalysts and results are shown in Fig. 6. All the samples exhibited diffraction peaks at 2θ = 28.70°, 33.21°, 47.62°, and 56.41° indexed to the (111), (200), (220), and (311) planes of the cubic fluorite CeO_2 structure (JCPDS 81–0792). The diffraction peaks at 2θ = 23.52°, 33.87°, and 41.16° in Fig. 6(a) could be indexed to the KNO_3 structure (JCPDS 74–2055). The diffraction peaks of KNO_3 had become weaker after three TPO cycles due to the redispersion of KNO_3 over CeO_2 in the reaction and the partial decomposition of KNO_3 to KNO_2 or K_2O as indicated by the TG-DTA results (Fig. 3). Figure 6(b) shows the XRD patterns of the 23 wt% $K/(K_2CO_3+CeO_2)$ catalyst. The diffraction peaks at 2θ = 30.72° and 31.72° from the sample before the first cycle were ascribed to K_2CO_3 (JCPDS 71–1466) and diffraction peaks at 2θ = 24.23°,

30.10°, 31.47°, and 39.25° from the used sample were ascribed to $KHCO_3$ (JCPDS 70–1167) instead of K_2CO_3. These results suggest that the potassium chemical state affects the basicity of the surface and thus the tendency to form carbonates and subsequent increase of the catalytic activity. If the basicity of the support is too high the CO_2 generated during soot combustion irreversibly adsorbs on the support. Then the following reaction (K_2CO_3 + H_2O + $CO_2 \leftrightarrow 2\ KHCO_3$ [29]) occurred and leaded to a low catalytic activity and poor stability.

3　Conclusions

K and CeO_2 are a good combination to oxidize soot particles. It has been reasonably well established that K improves the catalytic activity due to its high mobility, favoring the contact with soot and increasing the surface mobility of oxygen species. The effect of potassium precursor on the catalytic activity of CeO_2 for soot oxidation can be interpreted in terms of potassium mobility and basicity. The lower the value of the melting point, the higher the compound mobility on the surface, thus the higher the probability of contact between the catalyst and the soot particles, consequently, resulting in an increase of the catalytic activity. The stronger the basicity of the catalyst, the slower the desorption of CO_2 produced in soot oxidation, consequently, resulting in a decrease of the catalytic activity and stability.

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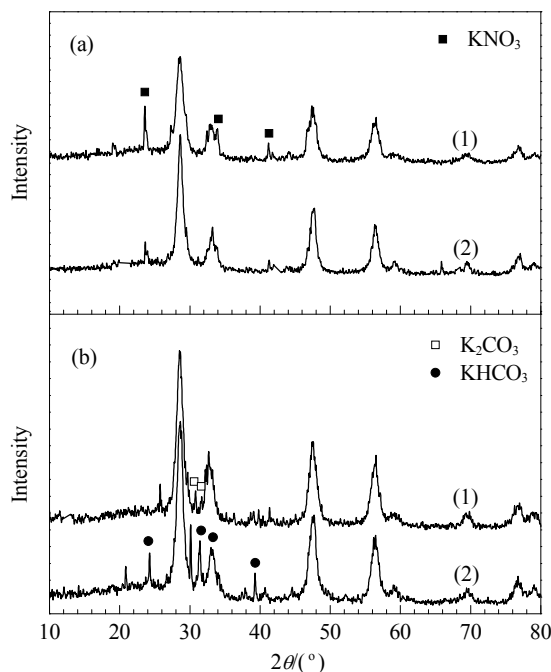12　Zaletova N V, Turakulova A O, Lunin V V. *Stud Surf Sci Catal*,

Fig. 6. XRD patterns of 19 wt% $K/(KNO_3+CeO_2)$ (a) and 23 wt% $K/(K_2CO_3+CeO_2)$ (b) catalysts. (1) Before cycle; (2) After cycle.

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