Efficient catalytic removal of diesel soot over Mg substituted

K/La_{0.8}Ce_{0.2}CoO₃ perovskites with large surface areas

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Abstract:

Mg-substituted La_{0.8}Ce_{0.2}CoO₃ (LCCM) perovskite oxides with large surface areas (148.7 m²/g) were prepared by a modified citric acid complexation method. Then, K promoted LCCM catalysts were synthesized via impregnation. The samples were characterized by XRD, FT-IR, N₂ adsorption-desorption, SEM, TEM, XPS and TG/DTA techniques. The addition of Mg not only restrained the growth of LCCM crystallite, but also inhibited the agglomeration of nanoparticles and, consequently the surface areas of LCCM perovskites increased. The low-valence ion substitution of Mg²⁺ both promoted the formation of Co⁴⁺ and adsorbed oxygen species, which were further enhanced by the partial replacement of La³⁺ by K⁺. The local electron density of neighboring carbon sites and their affinity for binding oxygen atom were promoted by K promotion, which also contributed to the contact between soot and catalyst surface, and the activity of the catalyst was thus enhanced. Among all the catalysts, the K/ LCCM-4 calcined at 600 °C exhibited the highest activity with $T_{m, t}$ at 380 °C, and

maintained good stability with $T_{m,1}$ only increased by 10 °C after recycling for three times.

Keywords: Diesel soot combustion; Catalytic removal; Perovskite oxides; Large surface area; KNO_3

1. Introduction

Soot particulate emissions from diesel exhaust have proven to be one of the serious environmental problems, which are deemed as an important source of particulate matter (PM) in air pollution[1]. Exhaust aftertreatment systems, consisted of diesel particulate filters and oxidation catalysts, have demonstrated to be effective for removal of the soot[2]. The key challenge is to develop highly active catalysts that can oxidize soot efficiently. Recently, various kinds of catalysts, such as precious metals[3, 4], alkali metal containing catalysts[5, 6], mixed oxides[7] and perovskite-type oxides[8, 9], have been developed for soot combustion. Among them, perovskite-type metal oxides have emerged as an important catalytic material because of their good redox properties, high thermal stability and good oxygen mobility[10]. The perovskite oxides possess a general formula of ABO_3 , where the activity of perovskite is based on the property of the B site elements because of their role in changing the electronic structure, and A site elements usually play the stabilizing role. During the last decades, lanthanum-based perovskite oxides have attracted increasing interest due to their low cost, good compositions/structures tunability and high thermal stability [11-12], and great efforts have been paid to the modification of A and/or B sites to develop perovskite oxides with better catalytic activities.

Rare earth elements, alkaline earth metals or alkaline metals are often added into the A

sites of perovskite oxides to enhance their catalytic performance. Cerium doped into perovskites can provide active oxygen species by a redox recycle between Ce^{4+} and Ce^{3+} , enhancing the oxygen storage capacity. However, excess doping amount of Ce would lead to distortion of the structure generating impurities phase, and restrain the increase of catalytic activity[8]. Low valence Mg^{2+} doped LaCoO_3 can enhance the mobility of surface lattice oxygen, change the valence of Co and generate oxygen vacancies during the reaction [9, 13]. Additionally, MgO can inhibit the sintering of the perovskite oxides.

The activity of perovskite oxides are limited by their low surface areas, usually less than $10 \text{ m}^2/\text{g}$, which are mainly ascribed to the agglomeration of particles caused by high temperature treatment. Therefore, much effort has been aimed to develop perovskite oxides with large specific surface areas. For instance, the preparation of LaCoO_3 perovskite using SBA-15 as hard template by nanocasting increased the surface areas up to $100 \text{ m}^2/\text{g}$ [14]. Also, the Mg-doped LaCoO_3 compounds with surface areas of $64.1 \text{ m}^2/\text{g}$ have been prepared by a modified citrated sol-gel technique[13]. Three-dimensionally ordered macroporous (3DOM) La-based perovskite catalysts with large pore sizes(>50 nm)were successfully prepared by the colloidal crystal templating method and employed for soot combustion. The surface areas of 3DOM perovskite materials reached $39 \text{ m}^2/\text{g}$ [12, 15].

The presence of alkali promoter, such as potassium, can evidently improve the soot oxidation activity of perovskite catalysts by improving the contact between the soot particles and the catalytic active sites[16]. Kim et al.[17] have found that K_2CO_3 supported on perovskite oxide presented a good catalytic activity for soot combustion. Peralta et al.[18] have reported the influence of K precursor on soot combustion, the activity of $\text{K}/\text{La}_2\text{O}_3$ for

soot oxidation followed the subsequent order: $\text{KNO}_3/\text{La}_2\text{O}_3 > \text{KOH}/\text{La}_2\text{O}_3 > \text{KCO}_3/\text{La}_2\text{O}_3$. Many studies have found that KNO_3 supported catalysts showed a high activity on soot combustion due to the high mobility of potassium[5, 19]. Therefore, KNO_3 supported on lanthanum-based perovskite oxides with high activity are attainable.

In this work, Mg substituted $\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ (LCCM) perovskite oxides with high surface areas were prepared by modified citrate sol-gel technique, and KNO_3 was supported onto LCCM by impregnation. The influences of Mg and K addition on the structure of LCCM perovskite catalysts were characterized by XRD, FT-IR, N_2 adsorption-desorption, SEM, TEM, XPS and TG/DTA techniques. The role of large surface area and K promotion on the catalytic performance of catalysts for soot combustion were investigated in detail.

2. Experimental

2.1. Catalyst preparation

2.1.1 Synthesis of Mg substituted $\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ perovskite catalysts

Mg substituted $\text{La}_{0.8}\text{Ce}_{0.2}\text{CoO}_3$ perovskite catalysts were prepared by the modified citrate sol-gel technique[13]. The corresponding nitrate salts were dissolved in deionized water to obtain an aqueous solution of La^{3+} , Ce^{2+} , Co^{2+} and Mg^{2+} with the expected stoichiometry. The molar ratio of La^{3+} to Mg^{2+} was set at 0.8: 0.1, 0.8: 1 and 0.8: 4, respectively. Then, appropriate amount of citric acid was added into the above solution as ligand, and the resulting solutions were evaporated at 75 °C to form a wet gel with vigorous stirring, which was subsequently dried at 110 °C for 12 h. After heating at 200 °C for 4 h and 400 °C for 2 h sequentially, the precursor was calcined at 700 °C for 4 h. The excessive amount of MgO was removed by dispersing the mixture in 0.2M acetic acid for 1h under vigorous stirring. At last,

the products were washed with deionized water, centrifuged and dried at 110 °C. The samples with La³⁺ to Mg²⁺ molar ratio of 0.8: 0.1, 0.8: 1 and 0.8: 4 were referred to as LCCM-0, LCCM-1 and LCCM-4, respectively.

2.1.2 Synthesis of K/LCCM perovskite catalysts

The K-promoted LCCM perovskites were prepared by impregnation using KNO₃ as precursor. LCCM perovskites were added to KNO₃ solutions in order to obtain 10 wt% loading of K. The suspension was evaporated while being vigorously stirred at 90 °C until the paste was formed. The above paste was dried at 110 °C for 12h, and then calcined at 400 or 600 °C for 3h. The sample supported on LCCM-0 or LCCM-4 was denoted as K/LCCM-0 or K/LCCM-4, respectively. The calcination temperature was labeled in the parenthesis after the catalysts.

2.2. Catalyst characterization

X-ray diffraction(XRD) patterns were recorded on a SmartLab-9 (RigaKu Corporation, Japan) automated power X-ray diffraction meter operating at 100 mA and 40 kV using Cu K α (λ = 0.1541 nm) radiation. The data of 2 θ from 20 to 80° were collected with a step scan of 0.02°.

FT-IR spectra were collected on a Nicolet-6700 spectrometer from Thermo Electron with a resolution of 5 cm⁻¹ using anhydrous KBr (Nicolet, United States) as dispersing agent.

Scanning Electron Microscopy (SEM) was taken on a Hitachi S4800 field-emission SEM instrument operated at 5 kV.

X-ray photoelectron spectroscopy (XPS) spectra were recorded on a PHI-5000 spectrometer using Al K α (1486.6 eV) radiation as the excitation source. All binding energies

were referenced to the C 1s peak at 284.5 eV, Gaussian–Lorentzian and Shirley background was applied for peak analysis.

A Perkin-Elmer Diamond TG/DTA instrument was used to obtain the weight loss and differential TG curves (DTG) of the samples. Each time, about 5 or 8 mg of the sample were heated at a constant rate.

2.3. Activity testing

Printex-U from Degussa was used as model diesel soot. The catalytic activity of the prepared samples for soot combustion was evaluated by TG/DTA under the tight contact (TC), and Temperature-Programmed Oxidation(TPO) reactions under the loose contact (LC) mode, respectively. Under the TC mode, the soot was mixed with catalyst in a weight ratio of 1:9 by grinding in an agate mortar for 10 min. The above mixtures were heated from 100 °C to 700 °C at 10 °C/min heating rate in a flow of synthetic air (20% O₂ and 80% N₂, 50 ml/min). Under the LC mode, the catalyst and soot were carefully mixed by spatula for 10 min, and then, were placed in the center of a cylindrical quartz tube reactor (8mm internal diameter). The reaction temperature was ranged from 200 °C to 600 °C with a heating rate of 1 °C/min, and the flow rate of feed gas (20% O₂ and 80% N₂) was set to 50 ml/min. The temperature for maximal soot combustion rate ($T_{m,1}$) under the TC mode and the temperature for maximum CO₂ concentration ($T_{m,1}$) under the LC mode were used to evaluate the catalytic performance of the catalysts. The stability of the catalyst was also tested by TPO under the LC mode.

3. Results and discussion

3.1. Catalysts characterization

The XRD pattern of LCCM and K/LCCM catalysts are shown in Fig. 1. The main

diffraction peaks of all catalysts are in good agreement with the crystalline structure of perovskite LaCoO_3 (JPCDS 48-0123), indicating that the perovskite structure is well maintained after Mg^{2+} doping and K^+ promotion. The intensity of LCCM perovskite main diffraction peak decreases with the increasing of excessive Mg^{2+} amount. The weak peak corresponding to CeO_2 ($2\theta=28.2^\circ$) is also detected in addition to the diffraction peaks of perovskites, which demonstrates the incorporation of Ce^{4+} into the perovskite oxides. As presented in Fig. 1(b), the (110) diffraction peak shifts to lower angle with the increasing amount of Mg-substitution, while the (110) diffraction peak shifts to higher angle after K^+ impregnation, indicating that both Mg^{2+} and K^+ are partially incorporated into the perovskite-type structure of catalysts[9,20]. The intensity of the (110) diffraction peak of K/LCCM-4(600) is also higher than that of K/LCCM-4(400), which shows that higher calcination temperature will facilitate the partial incorporation of K^+ into the perovskite structure to replace La^{3+} . The average crystal size calculated with the Scherrer equation from the broadening of XRD peak is shown in Table 1. As the Mg/La molar ratio increases from 0.1 : 0.8 to 4 : 0.8, the average crystal size of LCCM catalysts decreases from 18.8 nm to 14.2 nm, and the surface area increases significantly from 9.2 m^2/g to 148.7 m^2/g . When excessive amount of Mg is added, the un-doped MgO serve as pinning particles to inhibit the growth of LCCM crystals, which will contribute to the increasing of surface area. However, the average crystal size of LCCM catalysts only decreases from 14.9 nm to 14.2 nm, while the surface area increases remarkably from 29.6 m^2/g to 148.7 m^2/g . This may be attributed to the subsequent removal of the excessive MgO by acetic acid washing, which also contributes to the increasing of surface area. The crystal size and surface areas of LCCM catalysts only

change slightly after KNO_3 is supported on the perovskite. The crystal size of K/LCCM-4 increases from 13.8 nm to 14.4 nm as the calcination temperature increases from 400 °C to 600 °C due to the growth of crystallite size with temperature, and the surface area correspondingly decreases from 55.6 m²/g to 37.2 m²/g.

Fig. 2 shows the FT-IR spectra of the as-prepared catalysts. Three vibration bands around 596 cm⁻¹, 560 cm⁻¹, and 424 cm⁻¹ are observed, illustrating that the perovskite-type structure of the as-prepared catalysts are well preserved and kept stable after Mg^{2+} doping and K^+ promotion. The two peaks around 596 cm⁻¹ and 560 cm⁻¹ are attributed to two types of stretching vibration of Co-O bond in the CoO_6 octahedron, and the band at 424 cm⁻¹ is assigned to Co-O bending vibration in the CoO_6 octahedron[21]. The downshifts to lower wavenumber of the vibration band around 596 cm⁻¹ with the addition of Mg^{2+} are ascribed to the presence of high-valent Co^{4+} , which are caused by partial replacement of La^{3+} by Mg^{2+} , because the interaction of the stretching vibration for Co^{4+} -O bonding are greater than those for Co^{3+} -O. The band around 667 cm⁻¹ assigned to Co_3O_4 phase is not detected, because only trace amount of Co_3O_4 is formed. The bands at 1385 cm⁻¹ and 825 cm⁻¹ presented on the K/LCCM-0 and K/LCCM-4 catalysts correspond to KNO_3 , demonstrating that a fraction of potassium remains as KNO_3 , which is consistent with the XRD results.

The surface characteristics of catalysts are important to their catalytic activity for soot combustion. Thus, XPS technique is used to investigate the composition and chemical state of different elements on the surfaces of the as-prepared catalysts, and the results are shown in Fig. 3 and Table 2. The XPS spectra of Co 2p for the as-prepared catalysts are shown in Fig. 3(a). It's detected that carbon, oxygen, magnesium, potassium (for K/LCCM), cobalt,

lanthanum, cerium are present on the catalyst surfaces as shown in Table 2. After K-promotion, both K/LCCM-4(400) and K/LCCM-4(600) have lower Co atomic concentration due to the impregnation of KNO_3 on the surface of LCCM-4, which are less than 0.2. The intensity of Co 2p binding energies is also low for K/LCCM-4(400) and K/LCCM-4(600), as shown in Fig. 3(a). Two main peaks corresponding to Co $2p_{1/2}$ and Co $2p_{3/2}$ levels are detected for LCCM series catalyst and K/LCCM-0(600). The distorted Co $2p_{3/2}$ peak confirms the presence of at least two cobalt valence states. The peak binding energy of LCCM-0 is 779.77 eV for Co $2p_{3/2}$, which is similar to that for Co^{3+} ions as reported in literature[22]. As the $\text{Mg}^{2+}/\text{La}^{3+}$ molar ratio increases from 0.1:0.8 to 4:0.8, the binding energy of Co $2p_{3/2}$ increases from 779.77 eV to 780.57 eV. According to the studies of Dupin et al.[23], the higher the oxidation state of elements, the greater the electron binding energy. Thus, Mg^{2+} substitution has generated the transformation from Co^{3+} to Co^{4+} with higher valence, because the low-valence substitution of Mg^{2+} could raise the B site valence of LaCoO_3 perovskite to neutralize its structure charge. The binding energy of Co $2p_{3/2}$ in K/LCCM-0(600) catalyst increase compared to LCCM-0, this phenomenon may be resulted from the partial incorporation of some K^+ into the perovskite, more Co^{4+} is generated and stabilized by the partial replacement of La^{3+} with K^+ ions, as demonstrated by XRD results.

The XPS spectra of O 1s for the as-prepared catalysts are shown in Fig. 3(b). Two binding energy peaks in each spectrum corresponding to two kinds of oxygen species are observed. The O 1s with low binding energy is assigned to the lattice oxygen (O^{2-} , denoted as O_{lat}), while the other one with higher binding energy is attributed to the adsorbed oxygen species (such as O^- , O_2^- and O_2^{2-} , denoted as O_{ad})[22]. For LCCM samples, the percentage of adsorbed

oxygen to the lattice oxygen increases with the increase of excess MgO amount. This phenomenon can be explained by the high surface area of LCCM perovskite oxides, which could significantly enhance the adsorption capability of O_{ad} [13]. The adsorbed oxygen species(O_{ad}) are important for catalytic soot combustion, which are usually deemed as the origin of the characteristic catalytic properties for soot combustion. The adsorption capability of oxygen is further enhanced after supporting of KNO_3 , which demonstrates that the large number of oxygen vacancies may be formed by partially substitution of La^{3+} with K^+ , as illustrated by XRD and FT-IR characterization. What's more, the K/LCCM with large surface area possesses higher adsorption capability of oxygen than that with low surface area. According to the data in Table 3, the relative amount of adsorbed oxygen species for different samples follows the sequences of K/LCCM-4(600)> K/LCCM-4(400)> LCCM-4> K/LCCM-0(600)> LCCM-1> LCCM-0. Among all the catalysts, the K/LCCM-4(600) possesses the largest amount of adsorbed oxygen species.

The morphology of as-prepared samples is displayed in Fig. 4. SEM images of Fig. 4(a) show that LCCM-0 samples are mainly consisted of spherical primary particles with a grain radius in the range of 80-120 nm. However, the particles size of LCCM-4 reduces to less than 50 nm as shown in Fig. 4(c). The excessive MgO acts as pinning particles to inhibit the crystal growth of LCCM, which contributes to the increasing of surface area. As shown in Table 1, the crystal size of LCCM only decreases from 14.9 nm to 14.2nm as Mg/La molar ratio increases from 1 : 0.8 to 4 : 0.8, while the surface area increases significantly from 29.6m³/g to 148.7 m³/g. The pinning effect of MgO not only restrains the growth of crystal size, but also the agglomeration of nanoparticles. The LCCM-4 sample become cotton-like

after the excessive MgO is washed away by acetic acid, which also contribute to the increase of surface areas. After KNO₃ impregnation, the morphology of the K/LCCM-0(600) and K/LCCM-4(600) (see Fig. 4(b) and 4(d)) only change slightly, while the particles size grow larger. The smaller particles are favorable to achieve high surface area, which could evidently increase the amount of adsorbed oxygen species and facilitate the removal of soot particulates.

3.2. Catalytic soot combustion over as-prepared catalysts

The combustion of soot without catalyst under the TC mode is shown in Fig. 5(a) and Table 1, which clearly indicate that soot oxidation start at 476 °C and the $T_{m,t}$ is 607 °C when no catalyst is added. The performance of as-prepared catalysts for soot combustion under the TC mode is shown in Fig. 5(b) and Table 1, the $T_{m,t}$ of all catalysts reduce significantly after loading of catalysts. The LCCM-0 catalysts achieve good activity as the $T_{m,t}$ decreases to 432 °C. With the increase of excessive MgO amount, the activity of the catalysts is further enhanced, the $T_{m,t}$ of LCCM-1 and LCCM-4 catalysts are decreased to 421 °C and 399 °C, respectively. The activity of LCCM perovskite oxides are further enhanced after K⁺ promotion, with the $T_{m,t}$ of K/LCCM-4(600) down to 380 °C. It's noticed that both the support and calcination temperature have less influence on the $T_{m,t}$ of the K/LCCM catalysts under the TC mode, the activity of the as-prepared catalysts only change slightly, following the sequence of K/LCCM-4(600) > K/LCCM-4(400) > K/LCCM-0(600).

As the LC mode is more close to the actual soot combustion situation, the activity of as-prepared catalysts for soot combustion under the loose contact mode is shown in Fig. 6. It is obvious that the activity of all catalysts under the LC mode is lower than that under TC

mode. LCCM-0 catalyst can lower the $T_{m,1}$ to 478 °C, and the $T_{m,1}$ is further lowered with the increase in excess MgO amount, which is in good agreement with the TG-DTG results. When KNO_3 is supported on the perovskite, soot combustion is largely accelerated. The peak of CO_2 outlet concentration is changed from wide and low to steep and high, indicating the acceleration of the soot combustion rate. The K/LCCM-0(600) and K/LCCM-4(600) decrease the $T_{m,1}$ about 40 °C compared with that for LCCM-0 and LCCM-4. KNO_3 supported on the perovskite with large surface area possess much higher activity than that for conventional bulk perovskite with low surface area. Among all the K promoted catalysts, K/LCCM-4(600) shows the highest activity under the tight contact mode, while K/LCCM-4(400) exhibits the highest activity under the light contact mode, which lowers the soot combustion temperature by 227 °C. K/LCCM-4(400) possess higher specific surface areas than K/LCCM-4(600) (55.6 m^2/g versus 37.2 m^2/g), which means that surface area is more important to the activity of catalyst under the loose contact mode.

The catalytic stability of K/LCCM-4 under different calcination temperatures is studied by carrying out TPO experiments for three times. As shown in Fig. 7(a), the $T_{m,1}$ of K/LCCM-4(400) catalysts increase from 380 °C to 447 °C after reused for three times, the soot combustion rate also reduce as illustrated by the broadening of CO_2 outlet concentration peaks. Thus, the stability of K/LCCM-4(400) catalyst is not ideal. The TPO cycles profile of K/LCCM-4(600) catalyst is shown in Fig. 7(b). The $T_{m,1}$ only increases by 10 °C after recycling for three times, and the peak of CO_2 outlet concentration doesn't change remarkably. Thus, the K/LCCM-4 catalyst calcined at higher temperature shows higher catalytic stability. The stabilization phenomena of K-species under higher calcinations temperatures are also

observed for Fe-K/Al₂O₃ catalysts, which can be explained by the formation of more crystalline phase[24].

For the LCCM series catalysts, the catalysts with larger surface area possess more surface adsorbed oxygen species and Co⁴⁺ ions than that with smaller surface areas. Thus, the catalytic activity of the LCCM-0, LCCM-1 and LCCM-4 are gradually enhanced following the sequence of BET surface area growth. Compared with LCCM series catalysts, the K/LCCM series catalysts lower the $T_{m,1}$ much more than $T_{m,t}$. The adsorption capability of oxygen is further enhanced after K promotion. KNO₃ can increase the contact between soot and the surface of catalyst with the increase of possible effective collisions between soot and catalyst, which is generated by the melting of potassium nitrate on the catalytic surface[25,26]. Furthermore, the potassium can improve the catalytic activity of perovskite by the interaction of soot with the K⁺ ions on K/LCCM. As reported in literature, the K⁺ can act on π electrons of soot to form the covalent K-C bonds, the resulting electron transfer from soot to the electronegative oxygen may decrease the aromatic character of soot and activate gaseous oxygen[5, 27].

4. Conclusions

Mg²⁺ and Ce²⁺ substituted LaCoO₃ perovskites with K promotion were prepared and employed for soot combustion. The excessive MgO, which served as pinning particles to restrain the growth of LCCM perovskites crystallites and agglomeration of nanoparticles, could significantly increase the surface area of LCCM perovskites. The high surface area of LCCM perovskite oxides could significantly enhance the amount of adsorbed oxygen and further increase the catalytic activity. K promotion could increase the contact between soot

and the surface of catalyst by the melting of potassium nitrate on the catalytic surface. The K/LCCM-4(400) catalyst exhibited higher activity for soot combustion than K/LCCM-4(600) under the LC mode. However, the activity of K/LCCM-4(400) decreased remarkably after used for only three times. Comparatively, K/LCCM-4(600) maintained both high catalytic activity($T_{m, t}=380^{\circ}\text{C}$) and good stability.

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Table captions

Table 1 The list of specific surface areas (BET), crystal size, $T_{m,t}$ and $T_{m,1}$ of the samples.

Table 2 The atomic concentration of as-prepared catalysts.

Table 3 Binding energies (BE) of Co 2p_{3/2} and O 1s core levels and the percentage of adsorbed surface oxygen species(O_{ad}) for as-prepared catalysts.

Table 1 The list of specific surface areas (BET), crystal size, $T_{m,t}$ and $T_{m,l}$ of the samples.

Catalyst	$S_{BET}(m^2/g)$	Crystal size(nm)	$T_{m,t}(^{\circ}C)$	$T_{m,l}(^{\circ}C)$
LCCM-0	9.2	18.8	432	478
LCCM-1	29.6	14.9	421	467
LCCM-4	148.7	14.2	399	450
K/LCCM-0(600)	4.7	18.3	385	430
K/LCCM-4(400)	55.6	13.8	383	380
K/LCCM-4(600)	37.2	14.4	380	410

Table 2 The atomic concentration of as-prepared catalysts.

Catalyst	C 1s	O 1s	Mg 1s	K 2p	Co 2p	La 3d	Ce 3d
	(%)	(%)	(%)	(%)	(%)	(%)	(%)
LCCM-0	17.08	64.87	2.22	0.00	4.72	8.59	2.52
LCCM-1	23.41	61.45	1.98	0.00	2.86	6.26	4.05
LCCM-4	26.60	60.09	4.44	0.00	1.58	4.87	2.41
K/LCCM-0(600)	18.96	64.63	2.70	3.16	4.01	4.48	2.06
K/LCCM-4(400)	12.31	64.38	0.45	22.10	0.16	0.31	0.29
K/LCCM-4(600)	14.04	61.63	0.73	23.30	0.20	0.06	0.05

Table 3 Binding energies (BE) of Co 2p_{3/2} and O 1s core levels and the percentage of adsorbed surface oxygen species(O_{ad}) for as-prepared catalysts.

Catalyst	BE of C 1s (eV)	BE of Co 2p_{3/2}(eV)	BE of O 1s(eV)	Percentage of O_{ad} (%)
LCCM-0	284.49	779.77	531.0/528.5	58.7
LCCM-1	284.42	780.04	530.99/528.59	65.4
LCCM-4	284.28	780.57	530.84/528.36	81.6
K/LCCM-0(600)	284.36	780.03	531.3/528.64	67.1
K/LCCM-4(400)	283.94	-	531.85/528.64	95.1
K/LCCM-4(600)	284.24	-	531.78/528.5	98.8

Figure captions

Fig. 1. XRD patterns of LCCM and K/LCCM-4 catalysts: (a) the whole range and (b) the enlarged small range($2\theta=32^{\circ}$ - 34°)

Fig. 2. FT-IR spectra of as-prepared catalysts.

Fig. 3. XPS spectra of the as-prepared catalysts: (a) Co 2p and (b) O 1s.

Fig. 4. SEM images of different supporters and the supported catalysts: (a) LCCM-0; (b) 10%K/LCCM-0(600); (c) LCCM-4; (d) 10%K/LCCM-4(600)

Fig. 5. DTG profiles of soot combustion over prepared catalysts under the LC mode.

Fig. 6. The activity of as-prepared catalysts for soot combustion under the loose contact mode

Fig. 7. The TPO cycles profiles of K/LCCM-4 catalysts: K/LCCM-4(400) (a) and K/LCCM-4(600) (b).

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