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Three-dimensional ordered macroporous perovskite-type $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts with enhanced catalytic activity for soot combustion: the Effect of K-substitution

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ABSTRACT

Three-dimensional ordered macroporous (3DOM) $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ perovskite-type catalysts were successfully prepared by a colloidal crystal template method and characterized by scanning electron microscopy, transmission electron microscopy, high-resolution transmission electron microscopy, energy-dispersive X-ray scattering elemental mapping, X-ray diffraction, Raman and X-ray photoelectron spectroscopy, and temperature-programmed reduction of H_2 . Further, their catalytic activity in soot combustion was determined by temperature-programmed oxidation reaction. K substitution into the LaNiO_3 lattice led to remarkably improved catalytic activity of this catalyst in soot combustion. Amongst various catalysts, $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ exhibited the highest activity in soot combustion (with its T_{50} and S_{CO_2} values being 338 °C and 98.2%, respectively), which is comparable to the catalytic activities of Pt-based catalysts under the condition of poor contact between the soot and the catalyst. K-substitution improves the valence state of Ni and increases the number of oxygen vacancies, thereby leading to increased density of surface-active oxygen species. The active oxygen species play a vital role in catalyzing the elimination of soot. The perovskite-type $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ nanocatalysts with 3DOM structure without noble metals have potential for practical applications in the catalytic combustion of diesel soot particles.

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1. Introduction

In recent years, the problem of atmospheric pollution has become increasingly serious. Air pollution is not only tremendously disastrous to the ecological environment, but also significantly harmful to human health. An important source of atmospheric pollution is vehicle exhaust emission, particularly from diesel vehicles [1,2]. It is well known that soot particles emitted from diesel vehicles are the main source of $\text{PM}_{2.5}$ in urban air [3]. Catalytic after-treatment technology is one of the

most effective methods to reduce the emission of soot particles from diesel vehicles [4,5]. The technical goal is to find high-efficiency catalysts operating at low temperatures. Recently, a series of highly efficient catalysts for oxidizing diesel soot, such as noble metals [1,6], perovskite-like oxides [7], spinel-type oxides [8], and Ce-based oxides [9], have been reported. However, it is still challenging to realize catalytic soot combustion at the exhaust gas temperature (150–400 °C) [10].

The catalytic soot combustion is a complicated three-phase deep oxidation reaction involving solid (soot particles)-solid

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(catalyst)-gas (O_2 and NO) [11]. The catalytic activity of a catalyst in soot combustion is not only related to the intrinsic performance of the catalyst [12], but also to the contact efficiency between the solid catalyst and soot particles [13–15]. In our previous works, we found that a three-dimensionally ordered macroporous (3DOM) structure with large uniform pores (>50 nm) is a good way to improve the contact efficiency between the soot and catalyst, and we demonstrated the superior catalytic performance of 3DOM-structured catalysts in soot combustion [16–20]. For deep oxidation, the redox property of the 3DOM oxides is crucial to enhance their catalytic activity in soot combustion, and this is related to the surface active sites, which involves oxygen vacancies or coordinatively unsaturated metal cations for O_2 activation [21–23].

Perovskite-type composite oxides are a kind of potential catalyst for the catalytic oxidation reaction because of their excellent catalytic performance, stability, and low cost [24]. In the ABO_3 structure, A site is generally a rare earth element and B site is occupied by a transition metal element, which is regarded as the active site and can be influenced by the A site. Both A and B positions can be partially replaced by other metal ions of similar radii and the crystal structure of ABO_3 remains largely unchanged, with the formation of anion defects or change in the charge state of B-position ions. Compared to simple oxides, the perovskite-type structure with substituted A and B sites can cause some elements to exist in an abnormal valence state, creating a non-stoichiometric ratio of oxygen, or the active metal exists in a mixed valence state, which imparts some special physico-chemical properties and can adjust the density of the valences and lattice vacancies. In our previous studies, $LaMO_3$ (M: Ni, Co, Mn, Fe, Cr) perovskite-type oxide catalysts showed high catalytic activity in soot oxidation, and the catalytic activity of $LaNiO_3$ nanoparticles was found to be the highest among the catalysts [25]. We also found that the A-site cation in the perovskite structure substituted by an alkali metal (Li, K and Cs) can increase the number of oxygen vacancies and improve the catalytic activity of this catalyst in soot combustion, and the K ion is the best element to be substituted at the A site. In recent years, the effects of single atomic K and Cs substitution on the metal activity and reactive oxygen species in the catalyst have been reported [26,27]. Therefore, the design and synthesis of 3DOM $La_{1-x}K_xNiO_3$ perovskite-type oxide catalysts with good contact efficiency and highly active sites are promising to enhance their catalytic activity in soot combustion.

In this study, 3DOM $La_{1-x}K_xNiO_3$ perovskite-type oxide catalysts with different K doping concentrations were successfully fabricated via a one-pot method using a colloidal crystal template. 3DOM $La_{1-x}K_xNiO_3$ catalysts, which combine the good contact efficiency between the reactants and catalysts and optimal O_2 activated property, exhibited excellent catalytic performance in soot oxidation under the condition of poor contact between the soot and the catalyst. The effect of the 3DOM structure and K^+ substitution at the A-site (La^{3+}) on the catalytic performance of the catalyst in soot combustion was systematically investigated.

2. Experimental

2.1. Synthesis of the catalysts

3DOM $La_{1-x}K_xNiO_3$ catalysts were prepared via the colloidal crystal template (CCT) method using monodisperse poly(methyl methacrylate) (PMMA) microspheres, according to a synthesis and assembly method described previously [28]. Fig. 1 shows the typical procedure for the preparation of 3DOM $La_{1-x}K_xNiO_3$ catalysts with different amounts of substituted K. Stoichiometric amounts of the precursors, lanthanum nitrate, nickel nitrate, and potassium nitrate, were dissolved in ethylene glycol and methanol to obtain a homogenous solution. Then, a known amount of PMMA microspheres was added to the solution and the mixture was allowed to stand undisturbed for 5 h. After the immersion of the PMMA microspheres, the excess precursor solution was removed by suction filtration using a Bush funnel. The mixture of PMMA-CCT filled with the metal oxide precursors was further dried at 50 °C in an oven for 24 h. The dried mixtures were first calcined at 300 °C for 3 h and then cooled to room temperature under nitrogen. Afterwards, they were calcined again by increasing the temperature at the rate of 1 °C min⁻¹ in air and then maintaining at 650 °C for 4 h. Finally, a series of 3DOM $La_{1-x}K_xNiO_3$ perovskite-type catalysts ($x = 0.01, 0.05, 0.10$, and 0.20) were obtained.

2.2. Characterization

The morphology and microstructure of the catalyst were directly observed using a field emission environment scanning electron microscope (SEM) (FEI Quanta 200F, USA). The microstructures of the nanocatalysts were observed using transmission electron microscope (TEM, JEOL JEM LaB₆ 2100 electron microscope and FEI Tecnai GF20). The specific surface area of the catalyst was analyzed by the N_2 adsorption-desorption analysis. The Brunauer-Emmett-Teller (BET) characteristics and specific surface area of the prepared catalysts were carried out on a TriStar II Model 3020 adsorption desorber. The phase and unit cell structures of the synthesized catalysts were analyzed by powder X-ray diffraction (XRD) carried out on an XRD-6000 diffractometer (Shimadzu Corporation, Japan). The obtained XRD pattern was compared with a standard pattern to determine the phase composition of the

Fig. 1. Schematic illustration of the catalyst preparation.

catalyst. To obtain structural information of the catalyst and study the surface species, Raman spectra were recorded on a InVia Reflex–Renishaw Raman microscope with 532 nm He–Gd laser as the excitation source. X-ray photoelectron spectroscopy (XPS) was mainly used to analyze the surface element composition, valence charge, and chemical species present in the catalyst. XPS was carried out on K-Alpha type XPS (Thermo Fisher Scientific, USA), using Mg $K\alpha$ ($h\nu = 1253.6$ eV) as the excitation source, and C 1s signal (binding energy = 284.6 eV) was used as the standard to calibrate the gas element. Temperature-programmed reduction of H_2 (H_2 -TPR) is a type of temperature-programmed analysis that is generally suitable for evaluating the redox performance of a catalyst. The H_2 -TPR test was performed on an Autosorb IQ type physicochemical adsorption apparatus from Quantachrome, USA. The experimental procedure is as follows: 50 mg of the catalyst was fixed in a quartz reaction tube (diameter, 6 mm) using quartz wool to form a fixed bed. The catalyst was pretreated at 300 °C for 0.5 h in N_2 and subsequently cooled to 30 °C. 10% H_2/N_2 (50 ml min^{-1}) was flown on the catalyst bed heated at the rate of 10 °C min^{-1} in the temperature range of 30–800 °C. A thermal conductivity detector was used to monitor the H_2 consumption with an increase in temperature.

2.3. Evaluation of the catalytic performance

The catalytic activity of the catalyst in soot combustion was evaluated via a temperature-programmed oxidation (TPO) reaction. The soot model used is Printex-U commercial soot (92.0% C, 0.7% H, 3.5% O, 0.1% N, 0.2% S, and 3.5% of other impurities) produced by the Degussa company. A custom-made fixed bed microreactor was used. The catalyst to be tested was uniformly mixed with the soot particles (at the weight ratio of the catalyst to soot of 10:1) using a key to form a loose contact and then placed in a quartz reaction tube with an inner diameter of 6 mm. The mixed sample was placed in a constant temperature section of the reaction tube in a heating tube furnace and both ends were closed with quartz wool. The temperature of the furnace was controlled using a precision temperature controller and the heating rate was 2 °C min^{-1} . The reaction atmosphere consisted of 5% O_2 , 2000 ppm NO, and N_2 used as a balance gas, and the total flow rate was 50 ml min^{-1} . The product of the reaction outlet was detected by a gas chromatograph (GC, Sp-3420, Beijing) with an FID detector equipped with a methane conversion oven.

The catalytic activity during soot combustion is represented by the combustion temperature of the soot particles. The lower the temperature is, the higher the catalytic activity is. The catalytic activity was evaluated by the T_{10} , T_{50} , and T_{90} values, which are defined as the temperatures corresponding to 10, 50, and 90% soot conversion, respectively. These values are calculated by integrating the concentration of CO_2 and CO produced by the combustion of soot particles in the TPO reaction using the concentration versus temperature plot. In addition, in the soot combustion, the selectivity of CO_2 production (S_{CO_2}) is also an important indicator of the catalytic activity, which can avoid secondary pollution by the CO product. The selectivity of CO_2

production is calculated using the following formula:

$$S_{CO_2} = \frac{[CO_2]_{OUT}}{[CO_2]_{OUT} + [CO]_{OUT}} * 100\%$$

3. Results and discussion

3.1. SEM imaging

The morphology and spatial structure of the catalysts were observed using SEM and TEM. Fig. 2 exhibits the SEM images of PMMA-CCT and 3DOM $La_{1-x}K_xNiO_3$ catalysts. As shown in Fig. 2(a), the prepared PMMA-CCT forms a closely packed face-centered cubic cluster and the PMMA microspheres are uniform with a size of ~350 nm. As shown in Fig. 2(b–f), 3DOM $La_{1-x}K_xNiO_3$ catalysts have an ordered macroporous structure with an interconnected macroporous framework. 3DOM structures are derived from the long-range replication of the three-dimensionally close-packed PMMA template. The average pore size of the skeleton surrounding the uniform close-packed periodic voids is ~260 nm, which corresponds to a shrinkage of 20%–30% in comparison to the initial size of the PMMA microspheres, and the shrinkage is caused by the melting of the polymer template and the sintering of the produced metal oxide during the calcination steps used for removing the CCT. The macroporous structure is three-dimensional and it consists of small holes between each layer, which forms a three-dimensional network with internal cross-linking. The second layer of the 3DOM structure is clearly visible in the SEM images, and the uniform voids are interconnected via open windows with 80 nm diameter. In addition, the wall thicknesses of 3DOM $La_{1-x}K_xNiO_3$ catalysts observed from SEM images are ca. 30 nm. The 3DOM structure with good open spaces would effectively promote the contact efficiency between the

Fig. 2. SEM images of PMMA-CCT and 3DOM $La_{1-x}K_xNiO_3$ catalysts. (a) PMMA-CCT; (b) $LaNiO_3$; (c) $La_{0.99}K_{0.01}NiO_3$; (d) $La_{0.95}K_{0.05}NiO_3$; (e) $La_{0.90}K_{0.10}NiO_3$; (f) $La_{0.80}K_{0.20}NiO_3$.

soot and catalyst.

3.2. TEM and HAADF-STEM imaging

In order to further investigate the morphology and structure, a typical 3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ catalyst was observed by TEM and HRTEM (Fig. 3). Clearly, the 3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ catalyst has a regular structure with uniform pore diameter and good tunneling property. There are four clearly visible small holes under each large hole. The diameter of the window is ~ 80 – 120 nm. The existence of small holes creates a three-dimensional through-hole topology among the large holes. The structure reflects the close packing arrangement among the microspheres in the CCT. The 3DOM structure is favorable for the diffusion and propagation of solid particles into the interior of the catalyst, and this can increase the contact efficiency between the catalyst and solid reactant. As shown in Fig. 3(B), the lattice spacing of the 3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ catalyst was measured to be 0.381 and 0.272 nm, which corresponds to the (101) and (110) crystal planes, respectively, of the perovskite-type $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ oxide with a rhombohedral structure.

Fig. 4 shows the HAADF-STEM image and EDX-elemental mapping analysis of La, Ni, O, and K elements of a typical 3DOM $\text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3$ catalyst obtained to investigate the elemental composition and its distribution in the catalyst. HAADF-STEM image in Fig. 4(A) shows the structure of 3DOM with ordered pores (black) and framework (white). As is shown in Fig. 4(B), the elemental mapping images of La (green), Ni (yellow), O (red), and K (orange) elements overlap in the same position, indicating that these elements are uniformly distributed in the 3DOM $\text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3$ catalyst, and the La element (A site) can be substituted with K in the lattice framework of the perov-

Fig. 3. TEM (A) and HRTEM (B) images of the 3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ catalyst.

Fig. 4. HAADF-STEM image (A) and EDX-elemental maps (B) for La (green), Ni (yellow), O (red), and K (orange) of the 3DOM $\text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3$ catalyst.

skite-type $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ catalyst. K-substitution at the La site in perovskite-type $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts can increase the number of oxygen vacancies acting as active sites for O_2 activation, which is promising to improve the catalytic activity in soot combustion.

3.3. N_2 adsorption-desorption isotherms

The N_2 adsorption-desorption isotherms were obtained to investigate the pore structure and surface areas of the 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts, and the results are shown in Fig. 5. The N_2 adsorption-desorption isotherm shows type II behavior in the Brunauer classification and a H3 hysteresis loop. The amount of N_2 adsorbed by the sample increased sharply at $P/P_0 > 0.8$, indicating that the sample has a macroporous structure. After the K-substitution of the La site in the perovskite-type $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts, the isotherms remain unchanged, indicating that the substitution of K ion does not influence the pore structure and surface areas. The surface areas of the 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts are calculated by the multi-point (BET method), and the results are listed in Fig. 5. The BET surface areas of the 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts are in the range of 24 – $27 \text{ m}^2 \text{ g}^{-1}$, indicating that the incorporation of K ions has a weak influence on the specific surface area of the catalyst.

3.4. XRD results

In order to investigate the crystal structure of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts, XRD was performed and the patterns are shown in Fig. 6. As shown in Fig. 6(A), the peaks of the 3DOM LaNiO_3 catalyst at 23.3° , 32.6° , 40.8° , 47.4° , 53.3° , 58.8° , 68.7° , and 78.2° can be indexed to (101), (110), (021), (202), (211), (122), (220), and (312) crystal planes, respectively, of perovskite-type LaNiO_3 with a rhombohedral ABO_3 structure (JPCD#34-1181). After K-substitution at the La site in the perovskite-type $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts, no new peak is clearly observed, indicating that the prepared catalysts are of a single phase and the incorporation of K ions did not change the phase structure. With an increase in degree of K-substitution ($x > 0.1$),

Fig. 5. N_2 adsorption-desorption isotherms of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts.

Fig. 6. XRD patterns of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts over different 2θ ranges ((A) 20° – 85° ; (B) 32° – 34°). (a) LaNiO_3 ; (b) $\text{La}_{0.99}\text{K}_{0.01}\text{NiO}_3$; (c) $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$; (d) $\text{La}_{0.90}\text{K}_{0.10}\text{NiO}_3$; (e) $\text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3$.

the weak peaks are observed at 37.3° and 43.3° . This indicates the formation of a small amount of NiO when La^{3+} ions were partially replaced by K^+ ions. As shown in Fig. 6(B), it is worth noting that with an increase in K^+ substitution, the position of the (110) crystal peak obviously shifted from 32.6° (LaNiO_3) to 32.8° ($\text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3$). This peak shift is a direct proof that K^+ cations substituted La^{3+} cations and thus enters the lattice of LaNiO_3 , resulting in a change in the lattice parameters due to the shrinkage of the NiO_6 octahedron and shortening of the Ni–O bond length [29]. This result is not consistent with those reported previously [30], possibly due to the expansion of the lattice spacing after the inhomogeneous incorporation of K, rather than the contraction of the NiO_6 octahedron caused by the substitution of single atomic K. This will result in increased oxygen vacancies on the surface of the 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts for O_2 activation and enhanced catalytic activity for soot combustion.

3.5. Raman spectra

Raman spectroscopy is a sensitive technique to obtain additional structural information regarding both the M–O bond arrangement and surface lattice defects because the Raman spectrum is dominated by lattice oxygen vibrations. The phase structures of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts were further investigated by Raman spectroscopy with 532-nm excitation light (Fig. 7). As shown in the Fig. 7, all the catalysts show an obvious Raman band located at 392 cm^{-1} , which is consistent with the reported Raman band of LaNiO_3 [31]. This Raman band is assigned to the symmetric breathing mode of oxygen atoms around the nickel ions (Ni–O–Ni). With the incorporation of K, the Raman band split into two peaks and it shifted to a higher wavenumber. Combined with the XRD results, this can be attributed to the change in the Ni–O bond caused by the incorporation of K, which suggests an increase in the Ni–O bond energy and hence shortening of the bond length. The results are consistent with those of XRD, indicating that K^+ substituted La^{3+} , resulting in increased valence state of Ni and contraction of the

NiO_6 octahedron.

3.6. XPS results

XPS is a good tool to investigate the valence state of surface elements and adsorbed oxygen species of the catalysts. Fig. 8 shows the XPS spectra of K, La, Ni, and O elements of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts. The K $2p$ spectrum (Fig. 8(A)) exhibits two peaks at 295.7 and 292.9 eV, which are assigned to the spin-orbit splitting, K $2p_{1/2}$ and K $2p_{3/2}$, of K^+ species, respectively. The peaks of La $3d_{5/2}$ (Fig. 8(B)) could be deconvoluted into two doublets corresponding to the oxide (La_2O_3) and hydroxide species [32], and they can be attributed to the La $3d_{5/2}$ peak of the La^{3+} closed shell, which splits into two peaks due to the electron transfer from the oxygen center into the empty $4f$ shell during ionization [33]. Fig. 8(C) shows the XPS spectrum of Ni $2p_{1/2}$. The Ni $2p_{1/2}$ peaks of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts can be divided into three peaks corresponding to different valence states of Ni. The peaks located at 872.3, 873.9, and 875.6 eV are assigned to Ni^{2+} , Ni^{3+} , and Ni^{4+} species, respectively [34]. These three $\text{Ni}^{>2+}$ species in an environment surrounded by oxygen ions coexisted on the surface of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ cat-

Fig. 7. Raman spectra of 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts (excitation wavelength, 532 nm). (a) LaNiO_3 ; (b) $\text{La}_{0.99}\text{K}_{0.01}\text{NiO}_3$; (c) $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$; (d) $\text{La}_{0.90}\text{K}_{0.10}\text{NiO}_3$; (e) $\text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3$.

Fig. 8. XPS spectra for K 2p (A), La 3d_{5/2} (B), Ni 2p_{1/2} (C), O 1s (D) of 3DOM. (a) LaNiO₃; (b) 3DOM La_{0.99}K_{0.01}NiO₃; (c) 3DOM La_{0.95}K_{0.05}NiO₃; (d) 3DOM La_{0.80}K_{0.20}NiO₃.

alysts, and the percentage of Ni⁴⁺ obviously increased with an increase in K-substitution (Table 1). Among the catalysts, 3DOM La_{0.95}K_{0.05}NiO₃ shows the highest percentage of Ni⁴⁺. The increasing amount of Ni⁴⁺ in perovskite-type oxides can lead to increased amounts of surface active oxygen species and good redox property. It is also worth noting that the percentage of Ni²⁺ over the 3DOM La_{0.80}K_{0.20}NiO₃ catalyst increased remarkably in comparison to that over other catalysts (Table 1), which might be attributed to the formation of NiO on the surface of the catalysts.

For deep oxidation reaction, the catalytic performance of a material is correlated to its capability to activate oxygen. It is generally believed that perovskite-type oxides are capable of desorbing two oxygen species, namely, surface-adsorbed oxygen (O₂²⁻/O⁻ and O₂⁻) species and lattice oxygen (O²⁻). The surface-adsorbed oxygen species are weakly chemisorbed and are the main source of active oxygen species for soot combustion, which is closely related to the surface oxygen vacancy of the perovskite-type oxides [35]. The amount of surface oxygen species depends on the nature of the B site ion and the A site

ion that is substituted by other ions. The O 1s XPS of 3DOM La_{1-x}K_xNiO₃ catalysts are shown in Fig. 8(D). The spectra can be fitted with peaks corresponding to four types of surface oxygen species [36]. The results of spectral deconvolution are listed in Table 2. The low-energy peak at ~528.3 eV can be ascribed to the lattice oxygen species (O²⁻) in the perovskite-type La_{1-x}K_xNiO₃ oxides. The peak at ~529.3 eV can be assigned to the surface peroxide species (O₂²⁻/O⁻) [37] and the peak located at 531.1 eV may be attributed to the surface superoxide species (O₂⁻) and/or surface hydroxyl species. The formation of surface-adsorbed oxygen species is related to the surface density of oxygen vacancies induced by the incorporation of low valence K at the A site in ABO₃ perovskite oxides [29]. The surface-adsorbed oxygen species, usually believed to be the active oxygen species, play a vital role in catalyzing the elimination of soot particles. An additional peak with a binding energy of 532.70 eV reflects surface-adsorbed H₂O species, which also play a key role in the oxygen content [38]. Thus, the quantification results reveal that the surface density of active oxygen species over the 3DOM La_{0.95}K_{0.05}NiO₃ catalyst obviously in-

Table 1

Surface composition and oxidation states of La, Ni, and O species derived from XPS analyses.

Catalyst (3DOM)	La species (%)		Ni species (%)			O species (%)			
	La(OH) ₃	La ₂ O ₃	Ni ²⁺	Ni ³⁺	Ni ⁴⁺	O ²⁻	O ₂ ²⁻ /O ⁻	O ₂ ⁻ /-OH	H ₂ O
LaNiO ₃	65.9	34.1	6.3	90.8	2.9	20.1	13.1	55.1	11.6
La _{0.99} K _{0.01} NiO ₃	66.3	33.7	10.4	86.5	3.1	19.4	13.8	57.4	9.4
La _{0.95} K _{0.05} NiO ₃	69.6	30.4	11.7	77.5	12.8	16.3	13.4	61.4	8.9
La _{0.80} K _{0.20} NiO ₃	68.2	31.8	29.3	58.6	12.1	17.7	13.2	60.7	8.4

Table 2

Catalytic activity and CO₂ selectivity of 3DOM La_{1-x}K_xNiO₃ catalysts and LaNiO₃ in soot combustion under the condition of loose contact in comparison with the data obtained without catalyst.

Catalysts	$T_{10}/^{\circ}\text{C}$	$T_{50}/^{\circ}\text{C}$	$T_{90}/^{\circ}\text{C}$	$T_m/^{\circ}\text{C}$	$S_{\text{CO}_2}/\%$
3DOM LaNiO ₃	300	374	415	382	97.2
3DOM La _{0.99} K _{0.01} NiO ₃	301	373	412	374	97.8
3DOM La _{0.95} K _{0.05} NiO ₃	289	338	372	341	98.7
3DOM La _{0.90} K _{0.10} NiO ₃	289	346	381	346	98.6
3DOM La _{0.80} K _{0.20} NiO ₃	296	357	393	359	98.2
Particle-type LaNiO ₃	334	407	456	414	97.1
No catalyst	456	584	643	609	65.2

creased in comparison to that over the 3DOM LaNiO₃ catalyst, which is promising for enhancing its catalytic activity in soot combustion.

3.7. H₂-TPR results

The reduction behavior of the prepared catalysts was studied via H₂-TPR measurements. H₂-TPR determines three kinds of characteristics: (1) the oxidation and reduction, i.e., the redox property of the metal ions in the sample; (2) the mobility of oxygen on the surface and in the bulk of the sample; (3) the stability of the catalyst in the reducing atmosphere with H₂. Fig. 9 shows roughly two peaks for the series of catalysts. For 3DOM LaNiO₃, there is a peak with a strange shape located at 481 °C, which is attributed to the appearance of the processed product, La₂Ni₂O₅ in the reduction process of LaNiO₃, in agreement with the results of previous studies [39]. The first peak is due to Ni³⁺→Ni²⁺ and the second peak is due to Ni²⁺→Ni⁰. It is worth noting that, after a part of the La cations in the 3DOM LaNiO₃ perovskite was substituted by K, the peak area of the first peak increased remarkably. In addition, the reduction temperature range of the first peak also broadened slightly. This may be attributed to an increase in the amount of lattice oxygen and adsorbed oxygen atoms after K-substitution. With a gradual increase in the amount of substituted K, a new peak appears at 336 and 345 °C for 3DOM La_{0.95}K_{0.05}NiO₃ and 3DOM La_{0.90}K_{0.10}NiO₃ catalysts, respectively. This may be attributed to the reduction in the high valence Ni species (Ni⁴⁺) owing to the substitution of La³⁺ (A site) by K⁺, which results in increased valence of the B site (Ni ions) from Ni³⁺ to Ni⁴⁺ and the for-

mation of La_{1-x}K_xNi_{1-2x}Ni_{2x}O₃ in order to offset the charge balance of K⁺-substitution. This is in accordance with the XPS results (Table 1) that the 3DOM La_{0.95}K_{0.05}NiO₃ catalyst shows the largest percentage of the high valence state of B-site ions and the highest surface density of adsorbed oxygen species, which can lead to the deformation of the perovskite octahedral unit cell and increased surface density of oxygen vacancies for enhancing the adsorption capacity for O₂. However, the reduction peak observed at a relatively low temperature (< 350 °C) over the 3DOM La_{0.80}K_{0.20}NiO₃ catalyst disappears, and the reduction peak corresponding to Ni³⁺ to Ni²⁺ shifts to a higher temperature from 370 to 408 °C. This is attributed to the formation and separation of surface nickel oxides from the perovskite-type La_{1-x}K_xNiO₃ oxides due to excessive K⁺-substitution, which is in agreement with the results of XRD. With a gradual increase in K substitution, the area of the reduction peak takes a maximal value. The total amount of H₂ consumed over the 3DOM La_{0.95}K_{0.05}NiO₃ catalyst is the largest, indicating that the substitution of K improves the reducibility of the catalyst. In summary, the reducibility order of the 3DOM catalysts is La_{0.95}K_{0.05}NiO₃ > La_{0.90}K_{0.10}NiO₃ > La_{0.80}K_{0.20}NiO₃ > La_{0.99}K_{0.01}NiO₃ > LaNiO₃. The K-substitution for La ions results in an increase in the high valence Ni⁴⁺ species, which can promote the formation of surface oxygen vacancies for the adsorption and activation of the gas-phase oxygen and improve the migration of the surface oxygen species. Thus, 3DOM La_{1-x}K_xNiO₃ catalysts with good redox property should show high catalytic activity in soot combustion.

3.8. Catalytic performances of the materials in the removal of soot particulates

The catalytic performance of the as-prepared 3DOM catalysts for soot combustion was evaluated by the TPO method. A reaction atmosphere of 5% O₂, 2000 ppm NO, and N₂ was used as the balance gas, and the total flow rate of the gas was 50 mL min⁻¹. The results of CO₂ concentration and soot conversion as a function of the reaction temperature over the La_{1-x}K_xNiO₃ catalysts and LaNiO₃ are shown in Fig. 10. Further, the values of T_{10} , T_{50} , T_{90} , T_m , and S_{CO_2} , which are used as indicators of the catalytic performance are listed in Table 2. The results of the combustion of soot particles without any catalyst are also shown for comparison. In the absence of the catalyst, the combustion temperature of the soot particles is high, with T_{50} being 584 °C and S_{CO_2} being 65.2%. Clearly, the 3DOM LaNiO₃ cata-

Fig. 9. H₂-TPR profiles of 3DOM La_{1-x}K_xNiO₃ catalysts. (a) LaNiO₃; (b) La_{0.99}K_{0.01}NiO₃; (c) La_{0.95}K_{0.05}NiO₃; (d) La_{0.90}K_{0.10}NiO₃; (e) La_{0.80}K_{0.20}NiO₃.

Fig. 10. CO₂ concentration (a) and soot conversion (b) as a function of reaction temperature over particle-type LaNiO₃ and 3DOM La_{1-x}K_xNiO₃ catalysts.

lyst has a better catalytic activity in soot combustion than particle-type LaNiO₃, which indicates that the 3DOM morphology can effectively improve the activity of the catalyst in soot combustion. After K-substitution, the catalytic activities of the 3DOM La_{1-x}K_xNiO₃ catalysts are significantly higher than that of 3DOM LaNiO₃ catalyst, which is related to the incorporation of K into the perovskite lattice. The incorporation of K increases the amount of oxygen vacancies and valence of the B-site ion in LaNiO₃ perovskite. The valence of the B-site ion increases, resulting in a shortened Ni–O bond length and increased Ni–O bond energy. All these factors lead to changes in the amount of lattice oxygen and reactive oxygen species. The number of reactive oxygen species on the catalyst directly affects the catalytic activity in the oxidation of soot. Among all the studied catalysts, 3DOM La_{0.95}K_{0.05}NiO₃ had the highest catalytic activity in soot oxidation, i.e., the values of T_{10} , T_{50} , T_{90} , T_m , and S_{CO_2} are 289, 338, 372, 341 °C, and 98.2%, respectively. The catalytic activity of 3DOM La_{0.95}K_{0.05}NiO₃ is as good as that of the noble metal Pt catalyst, which is the best catalyst reported so far for soot combustion under loose-contact condition. The catalytic activity of the 3DOM La_{1-x}K_xNiO₃ perovskite catalyst for the catalytic elimination of soot follows the order, 3DOM La_{0.95}K_{0.05}NiO₃ > 3DOM La_{0.90}K_{0.10}NiO₃ > 3DOM La_{0.80}K_{0.20}NiO₃ > 3DOM La_{0.99}K_{0.01}NiO₃ > 3DOM LaNiO₃ > particle-type LaNiO₃. This is roughly consistent with the results of H₂-TPR. With an increase in K-substitution (>0.1), the catalytic activity decreased. This might be because the amount of substituted K was too large, which results in the partial conversion of the perovskite into NiO, leading to a decline in the catalytic activity. At the same time, it is apparent that K could be substituted into the perovskite at an appropriate amount to increase the catalytic activity.

3.9. Discussion on the effect of the 3DOM structure and K-substitution on the catalytic activity in soot combustion

The catalytic soot combustion is a typical three-phase deep oxidation reaction involving solid (soot particles)-solid (catalyst)-gas (O₂ and NO). The contact efficiency between the soot and catalyst strongly influences the catalytic performance of the latter in soot combustion. As shown in Table 2, 3DOM

LaNiO₃ has a better catalytic performance in soot combustion in comparison to that of the traditional particle-type LaNiO₃ catalysts under loose contact. This result also proves that the catalytic soot combustion is a structure-sensitive reaction. The 3DOM materials with a uniform pore size (>50 nm) and periodic voids interconnected through open windows could increase the contact area between the catalyst and soot (~25 nm). The soot particles can enter the pores of the 3DOM La_{1-x}K_xNiO₃ catalysts with the assistance of the NO and O₂ gas flow, and the contact area between the soot and catalyst could be increased remarkably. At the same time, the 3DOM structure also increases the specific surface area of the La_{1-x}K_xNiO₃ catalysts and enhances the adsorption of NO and O₂ reactants, which results in improved catalytic activity in soot combustion.

The structural characteristic of the catalysts is only one of the controlling factors for improving the catalytic activity during diesel soot combustion. Based on the essence of deep oxidation reaction for soot combustion, the catalytic activity is dependent on the redox property of the catalysts. It is well known that ABO₃ perovskite oxides show good redox properties, which is related to the oxidation capacity of the B-site ions and the surface density of oxygen vacancies. Moreover, the property of the B-site ions can be influenced by that of the A-site ions. All these factors lead to changes in the amount of active oxygen species, which is the main factor affecting the activity of the catalyst in the deep oxidation reaction. As shown in Table 2, the catalytic activities and the amount of active oxygen species of 3DOM La_{1-x}K_xNiO₃ catalysts are significantly higher than those of the 3DOM LaNiO₃ catalyst. The strong redox ability of the Ni (B) site in the perovskite-type ABO₃ oxides depends on its d-electron structure [40]. After the substitution of low valence K at the A site, the valence state of the Ni ions obviously increased to maintain the charge balance. The Ni³⁺ species in the octahedron field of perovskite-type LaNiO₃ possesses both low-spin state ($t_{2g}^6e_g^1$) and high-spin state ($t_{2g}^5e_g^2$). Ni³⁺ species in the low-spin state ($t_{2g}^6e_g^1$) could lose one electron and convert to Ni⁴⁺ species with a low-spin state ($t_{2g}^6e_g^0$). The appearance of Ni⁴⁺ species contributes to the shrinkage of the Ni–O octahedron and the shortening of the Ni–O bond length, which leads to excellent redox property of the 3DOM La_{1-x}K_xNiO₃ catalysts owing to the formation of Ni³⁺ and Ni⁴⁺

pairs. This is confirmed by the results of H₂-TPR (Fig. 9). Further, the substitution of K for La ions also increases the number of oxygen vacancies as active sites for O₂ and NO activation, which can increase the amount of surface active oxygen species. In the process of catalyzing soot combustion, active oxygen species can oxidize soot to CO₂ (direct catalytic pathway) and NO to NO₂ as an intermediate during soot combustion (indirect catalytic pathway). Thus, as shown in Table 2, 3DOM La_{1-x}K_xNiO₃ catalysts with K exhibited higher catalytic activity in soot combustion compared to that of the 3DOM LaNiO₃ catalyst.

In addition, it is also noted that the substitution of A-site for K⁺ ions should be controlled within a certain amount. Based on the results of XRD, H₂-TPR, and TPO, only an optimal degree of K-substitution leads to improved catalytic activity in soot combustion. With an increase in K-substitution in 3DOM La_{1-x}K_xNiO₃ catalysts, the increase in the Ni⁴⁺ species is not enough to maintain the phase-structure stability of the perovskite-type ABO₃ oxides and the impurity phases of oxides such as NiO appear and increase. This results in decreased catalytic activity in soot combustion. In summary, 3DOM La_{1-x}K_xNiO₃ catalysts, which take advantage of both superior contact efficiency between the soot and catalyst owing to the 3DOM structure and the high density of active sites for O₂ activation owing to the effect of K-substitution, exhibited excellent catalytic performance in soot combustion. Further, the 3DOM La_{0.95}K_{0.05}NiO₃ catalyst shows the highest catalytic activity in soot oxidation, i.e., the *T*₅₀ value is 338 °C, which is comparable to the catalytic activities of Pt-based catalysts under the condition of poor contact between the soot and the catalyst. The perovskite-type La_{1-x}K_xNiO₃ nanocatalysts with the 3DOM structure and K-substitution without noble metals have potential for practical applications in the catalytic combustion of diesel soot particles.

4. Conclusions

A series of 3DOM perovskite-type La_{1-x}K_xNiO₃ catalysts was prepared and employed for soot combustion. The uniform 3DOM structure of 3DOM La_{1-x}K_xNiO₃ catalysts can promote the contact efficiency between the reactants (O₂, NO, and soot particles) and catalysts. K⁺ ions substituted for La³⁺ ions in 3DOM La_{1-x}K_xNiO₃ catalysts were uniformly distributed in the crystal lattice of the perovskite oxides, and they could improve the formation of oxygen vacancies and enhance the redox property. 3DOM La_{1-x}K_xNiO₃ catalysts, which take advantage of both good reactant-catalyst contact efficiency owing to the 3DOM structure and high catalytic activity for gas reactants (O₂ and NO), exhibit superior catalytic performance in soot oxidation under the condition of poor contact between the soot and the catalyst. Further, the catalytic activity of LaNiO₃ in soot combustion was remarkably improved by K-substitution. Among all the catalysts, 3DOM La_{0.95}K_{0.05}NiO₃ showed the highest catalytic activity in soot oxidation (i.e., the values of *T*₁₀, *T*₅₀, *T*₉₀, *T*_m, and *S*_{co₂} are 289, 338, 372, 341 °C, and 98.2%, respectively), which is comparable to the catalytic activities of Pt-based catalysts under the condition of poor contact between

the soot and the catalyst. The K-substitution improves the valence state of Ni and increases the number of oxygen vacancies, thus increasing the density of surface active oxygen species. The active oxygen species play a vital role in catalytic soot combustion. The perovskite-type La_{1-x}K_xNiO₃ nanocatalysts with the 3DOM structure and K-substitution without the usage of noble metals have potential for practical applications in the catalytic combustion of diesel soot particles. The facile preparation strategy and technology for creating the 3DOM structure are potentially applicable to other metal oxides. Finally, the incorporation of K illustrates a promising and efficient way to design high-performance catalyst.

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Graphical Abstract

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Three-dimensional ordered macroporous perovskite-type $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts with enhanced catalytic activity for soot combustion: the Effect of K-substitutionXuelei Mei, Jing Xiong, Yuechang Wei*, Chujun Wang, Qiangqiang Wu, Zhen Zhao, Jian Liu
China University of Petroleum-BeijingPreparation of $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ catalysts with a three-dimensional ordered macroporous structure and the effect of K-substitution on their catalytic performance in soot combustion are presented.

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三维有序大孔钙钛矿型 $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ 催化剂提高炭烟催化燃烧活性: K取代的作用

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摘要: 催化炭烟燃烧的本质是典型的固体(炭烟颗粒)-固体(催化剂)-气体(O_2 和NO)三相深度氧化反应。因此炭烟燃烧性能不仅与催化剂的本征活性有关, 同时也与催化剂和炭烟颗粒之间的接触效率有关。钙钛矿型(ABO_3)氧化物具有高热稳定性和高催化活性, 在钙钛矿型氧化物中A位通常为稀土元素, B位通常为过渡金属元素, 钙钛矿的A, B位离子都可以被半径相近的其他元素部分取代, 而且物相结构不发生变化。我们组前期研究发现, 用碱金属部分取代钙钛矿型氧化物中的A位, 可以有效提高其催化活性。同时发现三维有序大孔(3DOM)结构可以有效的增加催化剂与碳烟颗粒的接触效率。基于此, 本文利用胶体晶体模板法成功制备了3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ 钙钛矿型催化剂, 并采用SEM, TEM, HRTEM, Elements mapping, XRD, Raman, XPS和 H_2 -TPR等手段对其物理化学性能进行了表征, 进一步探讨K取代对3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ 催化剂炭烟催化燃烧性能的影响。

SEM和TEM照片显示, 制备的3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ 催化剂孔道三维有序贯通, 孔径均一, 孔壁厚度均匀, 每个大孔下面展示清晰可见的小孔窗, 大孔孔径大约为260 nm, 这有利于炭烟颗粒在气流的协助下进入催化剂的孔道之内, 从而提高炭烟与催化剂之间的接触效率。3DOM结构催化剂具有大的比表面积($24\text{--}27\text{ m}^2\text{g}^{-1}$), 且K的取代对其比表面积无太大的影响。XRD和Raman谱证实了催化剂的钙钛矿结构, 且K能够取代La并进入钙钛矿氧化物的晶格中。XPS和 H_2 -TPR表征发现, K

取代La之后, B位的Ni元素的价态有所提升, 表面活性氧物种密度增加, 其中3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ 催化剂具有最高的 Ni^{4+} 的含量和活性氧含量. 3DOM $\text{La}_{1-x}\text{K}_x\text{NiO}_3$ 催化剂展示了高的炭烟燃烧催化性能, 且K的取代能够明显促进其催化炭烟燃烧活性. 在松散接触条件下, 催化剂炭烟催化燃烧活性的顺序为: 3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3 > 3\text{DOM } \text{La}_{0.90}\text{K}_{0.10}\text{NiO}_3 > 3\text{DOM } \text{La}_{0.80}\text{K}_{0.20}\text{NiO}_3 > 3\text{DOM } \text{La}_{0.99}\text{K}_{0.01}\text{NiO}_3 > 3\text{DOM } \text{LaNiO}_3 > \text{particle-type } \text{LaNiO}_3$. 其中, 3DOM $\text{La}_{0.95}\text{K}_{0.05}\text{NiO}_3$ 催化剂展示了最高的炭烟燃烧催化性能, 其 T_{50} 和 S_{CO_2} 值分别为338 °C和98.2%, 这与Pt基催化剂活性相当. 另外, 对炭烟催化燃烧性能的影响因素进行了探讨: 一方面, 三维有序大孔结构有效提高催化剂活性; 另一方面, K元素的取代提高了Ni的价态, 从而提升了表面活性氧物种数量, 这对炭烟催化燃烧起着至关重要的作用.

关键词: 三维有序大孔材料; 镍酸镧; 钾; 钙钛矿; 炭烟燃烧

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