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Article

Low temperature molten salt synthesis of porous $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) microspheres with high catalytic activity for CO oxidation

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ABSTRACT

A molten salt method was developed to prepare porous $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) microspheres using hierarchical porous $\delta\text{-MnO}_2$ microspheres as a template in eutectic $\text{NaNO}_3\text{-KNO}_3$. X-ray diffraction patterns showed that single phase $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ with good crystallinity was synthesized at 450 °C after 4 h. Transmission electron microscope images exhibited that the $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ sample obtained at 450 °C after 4 h possessed a porous spherical morphology composed of aggregated nanocrystallites. Field emission scanning electron microscope images indicated that the growth of the porous $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ microspheres has two stages. SEM pictures showed that a higher calcination temperature than 450 °C had an adverse effect on the formation of a porous spherical structure. The $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ sample obtained at 450 °C after 4 h displayed a high BET surface area of 55.73 m^2/g with a pore size of 9.38 nm. Fourier transform infrared spectra suggested that Sr^{2+} ions entered the A sites and induced a decrease of the binding energy between Mn and O. The CO conversion with the $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) samples indicated that the $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ sample had the best catalytic activity and stability. Further analysis by X-ray photoelectron spectroscopy demonstrated that Sr^{2+} doping altered the content of Mn^{4+} ions, oxygen vacancies and adsorbed oxygen species on the surface, which affected the catalytic performance for CO oxidation.

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1. Introduction

Over the past several decades, catalytic oxidation of CO has attracted considerable attention due to its potential applications in many fields such as automobile exhaust, fuel cell technology, carbon dioxide laser and air purification in an enclosed atmosphere [1–3]. Among the catalysts suitable for this purpose, supported noble metals initially seemed to be good candidates. However, owing to high prices and low reserves of noble metals, nowadays, perovskite oxides such as the lanthanum manganites are potential substitutes for noble metal cata-

lysts because of their unique properties such as their catalytic activity for CO oxidation [4].

In the LaMnO_3 perovskite oxide, Mn^{3+} ions are coordinated with six oxide ions and the MnO_6 units are connected in a corner-sharing manner making networks in which La^{3+} ions are located in the dodecahedral sites of the framework [5]. Due to its structural flexibility, the La^{3+} and/or Mn^{3+} ions in the lattice can be partially replaced by foreign cations (transition or rare metal ions) with no large change in the crystalline structure to produce substituted perovskites [6]. This property has frequently been exploited because the substitution usually pro-

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motes catalytic activity [7–10]. Substitution of La^{3+} ions with a divalent metal cation is accompanied by a change of the oxidation state of the manganese ions, thus leading to a modification in the catalytic activity for CH_4 combustion [7]. Ponce et al. [8] studied the partial substitution Sr^{2+} for La^{3+} ions in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0\text{--}0.5$) oxides and found that with the substitution amount increasing, to balance the total charge, the charge compensation was achieved by the oxidation of Mn^{3+} to Mn^{4+} . The presence of Mn^{4+} cations in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ oxide enhanced the catalytic activity by influencing the active oxygen near the Mn^{4+} that takes part in methane oxidation [9]. Nevertheless, the substitution of Mn^{3+} ions in LaMnO_3 oxide proved to be a far more effective method to optimize the catalytic activity than choosing different lanthanides to substitute for La^{3+} ions in A sites. Geng [10] revealed that compared with partial substitution of A sites in $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ oxide with Sr^{2+} ions, the ignition temperature of $\text{LaMn}_{1-y}\text{Cu}_y\text{O}_3$ oxides with an equal substitution amount of B sites with Cu^{2+} ions was far lower in the catalytic oxidation of CO.

On account of the high catalytic activity of the substituted perovskite, many studies on the improvement of catalytic activity have been carried out. Among these, increasing the specific surface area was considered to be an effective strategy. Hence, different preparation routes and technical conditions such as a solid state reaction, sol-gel, hydrothermal treatment, spray-drying, freeze-drying, co-precipitation, chemical vapor deposition, microemulsion [11] and templates [12] have been used to prepare substituted perovskite catalysts with a high specific surface area to boost the catalytic performance for CO oxidation.

However, there have been few reports of perovskite-type oxides with specific morphologies prepared by the metal salt method. Liu et al. [13] reported that perovskite-type ACeO_3 ($A = \text{Sr}, \text{Ba}$) was synthesized by the metal salt method at low temperatures in eutectic NaCl-KCl . Chen et al. [14] revealed that the perovskite single crystalline LaMnO_3 nanocubes have been fabricated by a facile salt-assisted solution combustion process. Wang et al. [15] studied a morphology-controlled molten salt route developed to synthesize porous spherical LaMnO_3 and cubic LaMnO_3 nanoparticles using the as-prepared porous Mn_2O_3 spheres as a template.

In this work, first, hierarchical porous $\delta\text{-MnO}_2$ microspheres were synthesized by a hydrothermal reaction at 80°C . Then, in order to decide the optimal calcination temperature, the $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ catalysts were synthesized at different temperatures ($450, 550$ and 650°C) using the synthesized $\delta\text{-MnO}_2$ microspheres as a template in eutectic $\text{NaNO}_3\text{-KNO}_3$. Finally, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) catalysts obtained at the optimal calcination temperature were used to investigate the effect of Sr^{2+} doping on the catalytic activity for CO oxidation.

2. Experimental

2.1. Material preparation

All the chemical reagents were analytical purity and used without any further purification. Distilled water was used in the

synthesis and treatment processes.

Hierarchical porous $\delta\text{-MnO}_2$ microspheres were synthesized by a hydrothermal reaction. In a typical procedure [16], first, 0.9 g of KMnO_4 and 2 ml of $37\text{ wt\%}$ HCl were dissolved into 80 mL of distilled water at room temperature. After continuous magnetic stirring for 30 min , the homogeneous purple solution was sealed in a 100 mL Teflon-lined autoclave and maintained at 80°C for 10 h in an oven. After cooling down to room temperature, the products were separated by filtration, washed with distilled water and absolute ethanol several times, and then dried in an oven at 60°C for 12 h . The product was denoted as S80.

The spherical porous $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) catalysts, referred to as LSMF (X) ($0 \leq X \leq 0.6$), were prepared by the molten salt method, using the synthesized hierarchical porous $\delta\text{-MnO}_2$ microspheres as a template. A mixture of NaNO_3 and KNO_3 with a molar ratio of $1.5:1$ was adopted as the molten salt. Stoichiometric amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Sr}(\text{NO}_3)_2$, as-synthesized MnO_2 and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were well mixed and ground in an agate mortar for 20 min . The nitrate and as-synthesized MnO_2 to molten salt molar ratio was of $1:15$. Then, in order to decide the optimal calcination temperature, the $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ samples were heated at different temperatures ($450, 550$ and 650°C) with a heating rate of $5^\circ\text{C}/\text{min}$ for 4 h , respectively denoted as S450, S550 and S650. After cooling to room temperature in air, the products were immersed into deionized water in a beaker to transfer the product into an aqueous solution for the subsequent separation and purification. The remnant molten salts were removed from the products by washing with hot deionized water several times until there was no white precipitate on the surface. The synthesized products were finally dried at 80°C for 12 h . The $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) catalysts were synthesized at the optimal calcination temperature to investigate the effect of Sr^{2+} doping on the catalytic activity for CO oxidation.

2.2. Material characterization

Powder X-ray diffraction (XRD) patterns were obtained using a D/max-RB type X-ray diffractometer with a step size of 0.02° and $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418\text{ nm}$). The 2θ scan range was $10^\circ\text{--}80^\circ$. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer (Thermo, USA) using KBr pellets in the wavenumber range of $4000\text{--}400\text{ cm}^{-1}$. Scanning electron microscope (SEM) images were obtained on a JSM-IT300 electron microscope (JEOL, Japan). Field emission SEM (FESEM) and transmission electron microscope (TEM) analysis as well as the corresponding selected area electron diffraction (SAED) patterns were conducted on a Zeiss Ultra Plus-43-13 (German) and JEM-2100F electron microscope (JEOL, Japan), respectively. The specific surface area (A_{BET}) and porosity were determined by nitrogen adsorption isotherms at -196°C using a Micromeritics ASAP 2020 M sorption analyzer (USA). The Brumauer-Emmett-Teller (BET) model was applied for specific surface area determination and the Barrett-Joyner-Halanda (BJH) model was used for porosity characterization using the adsorption branches of the

isotherms. Sample analyses were performed after outgassing in vacuo (residual pressure $\sim 10^{-2}$ mbar) for 5 h at 120 °C. X-ray photoelectron spectroscopy (XPS) was obtained on an ESCALAB 250 Xi system (Thermo, China) using the monochromatized Al $K\alpha$ radiation ($h\nu = 1486.6$ eV) at room temperature and a vacuum of 10^{-7} Pa (10^{-9} Torr). The error of the binding energy was ± 0.2 eV and the C 1s ($E_b = 284.6$ eV) of the contaminated carbon was used as a standard for binding energy calibration.

2.3. Evaluation of catalytic activity

Catalytic performance for CO oxidation was examined in a fixed-bed quartz microcatalytic flow reactor (i. d. = 8 mm) at atmospheric pressure. The reactor was positioned in an electrical furnace provided with a thermocouple on its wall. The temperature of the reactor was maintained by a temperature controller. Approximately 100 mg catalyst powders mixed evenly with glass-asbestos (catalyst:glass-asbestos = 1:5) were loaded into the reactor in each trail. Carbon monoxide, oxygen and argon were regulated using mass flow controllers. The molar composition of the feed was CO/O₂/Ar (balance) = 1/1.25/97.75 and the total flow rate of the gas mixture was 438 mL/min giving a space velocity (GHSV) of 12000 h⁻¹. Catalytic runs were performed at temperatures ranging from room temperature to 250 °C. The system outlet was connected to a gas chromatograph (GC-7890 II, China) equipped with FID and TCD double detectors to separate reactants and products. The detected compounds were CO, O₂ and CO₂.

3. Results and discussion

Shown in Fig. 1 are the XRD results of the synthesized precursor and LaMn_{0.8}Fe_{0.2}O₃ samples by heating the mixture of nitrates and the precursor in the molten salt of NaNO₃ and KNO₃ at different temperatures for 4 h. It was clearly seen that there were only four very weak peaks indexed to pure layered

Fig. 1. XRD patterns of the samples. (1) S80; (2) S450; (3) S550; (4) S650.

birnessite-type MnO₂ (JCPDS 80-1098, monoclinic, $C2/m$, $a = 0.515$ nm, $b = 0.284$ nm, $c = 0.717$ nm) in Fig. 1(1). MnO₂ can form many polymorphs by interlinking the basic MnO₆ octahedra in different configurations. Birnessite-type MnO₂ with a two-dimensional (2D) lamellar structure is usually denoted as δ -MnO₂. Generally, layered birnessite-type MnO₂ needs more cations to stabilize the structure owing to an interlayer distance of 0.73 nm in the birnessite. The insertion/extraction of cations results in the coexistence of Mn⁴⁺ and Mn³⁺ ions in the δ -MnO₂. In addition, it was clearly observed that there was only the LaMn_{0.8}Fe_{0.2}O₃ phase similar to the cubic LaMnO₃ (JCPDS 75-440, $Pm-3m$, $a = 0.388$ nm) and no other impurity was detected (Fig. 1(2), (3) and (4)). With a rise in calcination temperature from 450 to 650 °C, the intensity of the diffraction peaks decreased significantly, indicating that in eutectic NaNO₃-KNO₃, single phase LaMn_{0.8}Fe_{0.2}O₃ can be generated from the mixture of nitrate and δ -MnO₂ at a low temperature and a further increase in sintering temperature was beneficial for the improvement of crystallinity.

The morphology of S80 from the hydrothermal reaction was obtained by FESEM and TEM. As shown in Fig. 2(a-1) and (a-2),

Fig. 2. FESEM images of (a-1, a-2) S80 and (b-1, b-2) S450; TEM images of (a-3, a-4) S80 and (b-3, b-4) S450.

S80 has a hierarchically porous structure consisting of 4.0 μm sized microspheres assembled from interleaving thin nanosheets in agreement with the study by Xiao et al. [17]. Seen from the TEM images (Fig. 2(a-3)), the darker/lighter contrast indicated that the microspheres clearly exhibited a core-corona structure and further demonstrated that pores exist not only on the surface but also in the interior. As can be seen from the HRTEM image in Fig. 2(a-4), an average lattice spacing was calculated to be 0.275 nm in good agreement with that (0.284 nm) of the (010) plane of $\delta\text{-MnO}_2$. From the corresponding SAED pattern (inset in Fig. 2(a-4)), one can see that there were only three weak diffraction spots, indicating that S80 with bad crystallinity is a single crystal in good agreement with the XRD results.

Fig. 2(b) shows the FESEM and TEM images of S450. Obviously, S450 still maintained the porous spherical structure composed of aggregated nanocrystallites and the size of the pores become smaller (Fig. 2(b-1)). The TEM image (Fig. 2(b-3)) further showed that these pores existed not only on the surface but also within the microspheres. In addition, the HRTEM image in Fig. 2(b-4) indicated that the lattice spacing of 0.27 nm was consistent with that (0.274 nm) of the S450 (110) plane and the single crystalline character is also demonstrated by the clear diffraction spots in the Fourier transform of a small well-ordered region (inset in Fig. 2(b-4)). However, as shown in Fig. 2(b-2), the hierarchically porous structure similar to $\delta\text{-MnO}_2$ was also found in S450 but the nanosheets were thicker and decorated with nanoparticles on the surface. Therefore, it can be deduced that the growth processes of the porous $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ microspheres included several stages. In the initial stage, $\text{La}(\text{NO}_3)_3$, $\text{Sr}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ dissolved into the salt and then diffused onto the surface of the nanosheets due to the much better solubility than the $\delta\text{-MnO}_2$ microspheres. Then the $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ phase was formed in situ and because of the preservation of the hierarchically porous spherical structure, the morphology of S450 resembled that of $\delta\text{-MnO}_2$. Finally, the nanosheets were gradually transformed into nanoparticles.

In order to further understand the effect of calcination temperature on the morphology of $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ oxides, the morphology of the products was observed by SEM. Fig. 3 gives the SEM images of S550 and S650. As observed from Fig. 3(a) and (b), in S550, part of $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ microspheres were smashed into semi-spherical or axiohitic particles, surrounded by agglomerated nanocrystallites. As the calcination temperature continued increasing to 650 $^\circ\text{C}$, fewer spherical $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ oxides were observed and part of the remaining spherical $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ oxide was covered with agglomerated nanocrystallites (Fig. 3(c) and (d)), indicating that the nanocrystallites were generated by peeling from the surface to the core of the $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ microspheres at the high temperature.

Fig. 4 shows the nitrogen adsorption-desorption isotherms and corresponding pore size distribution curves of the $\delta\text{-MnO}_2$ and $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ oxide obtained at different sintering temperatures. According to IUPAC classification, S80 and S450 samples showed a Type IV isotherm with H3 hysteresis loop in the relative pressure (p/p_0) range of 0.4–1.0 (Fig. 4(a)), indicating the existence of a mesopore structure [18]. The N_2 ad-

Fig. 3. SEM images of samples. (a, b) S550; (c, d) S650.

sorption quantity of S80 was higher than S450, suggesting a more porous structure and thus larger surface area and pore volume in the S80 [19], which was also confirmed by the results shown in Table 1. S550 and S650 gave a Type V isotherm with a very minor hysteresis loop at high relative pressures associated with a low pore volume (Fig. 4(c)). On the other hand, the isotherm shapes of the four samples differ from each other, also indicating that there exists differences in pore distribution. This deduction was substantiated by the results of the pore size distributions (Fig. 4(b) and (d)). For S80 and S450, the pore size distributions cover a wide range from 2 to 100 nm. In fact, the pores were mostly composed of mesopores (2–50 nm) and they also contain a small number of macropores (> 50 nm). Compared with S80, the average pore diameter of S450 was smaller. However, S550 and S650 both possessed two peaks including a sharp peak at 2.55 nm formed from aggregated nanocrystallites, and a weak peak covering a wider range from 12.5 to 125 nm, perhaps induced by the fracture of microspheres and collapse of the porous structure in fair agreement with the SEM results.

The textural parameters including the specific surface area, mean pore diameter and average pore volume are summarized in Table 1. Clearly, S450 has a larger specific surface area (55.73 m^2/g), average pore diameter (9.38 nm) and pore volume (0.37 cm^3/g). The specific surface area, average pore diameter and average pore volume decreased with the calcination temperature increase.

Fig. 5 shows the $X(\text{CO})$ curves of S450, S550 and S650. It can be clearly seen that for S450, S550 and S650, $X(\text{CO})$ increased with a rise in reaction temperature, and as the calcination temperature increased, the catalytic performance of $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ oxide decreased. Especially, for S650, $X(\text{CO})$ at 250 $^\circ\text{C}$ was less than 10% on account of a smaller surface area, which was detrimental to the adsorption of CO and O_2 molecules and the diffusion of adsorbed CO species and adsorbed oxygen species [20]. Nevertheless, compared with S450, the temperature (190 $^\circ\text{C}$) of 50% $X(\text{CO})$ (T_{50}) for S550 was 3 $^\circ\text{C}$ higher. Hence, a conclusion can be obtained that spherical porous $\text{LaMn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ oxide with a better CO oxidation activity was synthesized at 450 $^\circ\text{C}$ for 4 h in eutectic $\text{NaNO}_3\text{-KNO}_3$.

Fig. 4. Nitrogen adsorption-desorption isotherms (a, c) and pore size distribution curves (b, d) of samples.

To identify the effects of Sr^{2+} substitution amount on the catalyst structure, the FT-IR spectra of LSMF (X) ($0 \leq X \leq 0.6$) are shown in Fig. 6. The broad vibration band at 3404 cm^{-1} was attributed to the stretching vibration of the $-\text{OH}$ group from the water molecules [21]. The weak band at 1635 cm^{-1} was nor-

mally associated with the O–H bending mode and the peak at 1470 cm^{-1} corresponded to the bending vibration of O–H bonds connected to Mn atoms [22]. The sharp band at 1348 cm^{-1} as well as the peak at 850 cm^{-1} was assigned to the vibration of residual NO_3^- on the surface of the catalysts [23] and the peak at 1050 cm^{-1} was ascribed to *trans*- and *cis*-hyponitrite ($\text{N}_2\text{O}_2^{2-}$) species [24]. Besides, the FT-IR peaks in the range of $400\text{--}1000 \text{ cm}^{-1}$ revealed the existence of octahedral MnO_6 [25]. However, compared with the stretching vibration peak of Mn–O bond in the MnO_6 octahedron at 600 cm^{-1} in a previous study [26], the

Table 1

Textural properties of the samples.

Sample	Specific surface area (m^2/g)	Average pore diameter (nm)	Average pore volume (cm^3/g)
S80	86.76	11.97	0.61
S450	55.73	9.38	0.37
S550	33.95	7.37	0.16
S650	13.83	7.44	0.13

Fig. 5. Catalytic activities for CO oxidation over S450, S550 and S650.

Fig. 6. FT-IR spectra of the spherical porous LSMF (X).

Fig. 7. Catalytic activity for CO oxidation over the spherical porous LSMF (X).

peak at 530 cm^{-1} associated with the vibrations of Mn–O bonds was slightly shifted towards lower wavenumbers, which was assigned to Fe^{3+} ion doping [27]. Furthermore, with the Sr^{2+} substitution amount increasing, the peak intensity at 530 cm^{-1} trailed off gradually, indicating that Sr^{2+} ions had indeed entered A sites, inducing the binding force between Mn and O to decrease. In other words, as Sr^{2+} ions substituted for La^{3+} ions, to ensure electrical neutrality, the oxidation state of manganese ion would increase from Mn^{3+} to Mn^{4+} and there existed not only DE interactions of $\text{Mn}^{3+}\text{--O--Mn}^{3+}$ or $\text{Fe}^{3+}\text{--O--Mn}^{3+}$ but also $\text{Mn}^{3+}\text{--O--Mn}^{4+}$. As a result, the variation of the Mn–O bond length and angle led to the structural distortion of $\text{FeO}_6/\text{MnO}_6$ (BO_6) octahedrons [28], weakening the stability of octahedron

Table 2

Characteristic temperature for CO oxidation conversion with spherical porous LSMF (X) oxide as catalyst.

Sample	T_{50} (°C)	T_{90} (°C)
LSMF (0)	187	198
LSMF (0.15)	186	198
LSMF (0.3)	185	198
LSMF (0.45)	<125	181
LSMF (0.6)	<<125	<125

structure.

Fig. 7 gives the results of the spherical porous LSMF (X) ($0 \leq X \leq 0.6$) oxide for CO catalytic oxidation. It is evident that a little substitution of Sr^{2+} for La^{3+} ions can slightly improve the catalytic activity for CO oxidation, while the catalytic activity was greatly improved when the substitution amount was more than 30%. As shown in Table 2, for LSMF (X) ($X = 0, 0.15, 0.3$), 50% $X(\text{CO})$ was achieved at $186\text{ }^\circ\text{C}$ and 90% $X(\text{CO})$ was achieved at $198\text{ }^\circ\text{C}$. However, for LSMF (X) ($X = 0.45, 0.6$), T_{50} values were both far below $125\text{ }^\circ\text{C}$. The temperature of 90% $X(\text{CO})$ (T_{90}) of LSMF (0.6) was still less than $125\text{ }^\circ\text{C}$, while the temperature of LSMF (0.45) was $181\text{ }^\circ\text{C}$. T_{90} of LSMF (X) ($X = 0.45, 0.6$) was less than $275\text{ }^\circ\text{C}$ in our previous study [10] and T_{90} of LSMF (0.6) was lower than that ($175\text{ }^\circ\text{C}$) in Ref. [20]. This indicated that when the substitution amount of Fe^{3+} for Mn^{3+} ions in the B sites was 20%, it greatly enhanced $X(\text{CO})$ through increasing the substitution amount of Sr^{2+} for La^{3+} ions in the A sites (more than 30%). This is because of the formation of more Mn^{4+} ions and oxygen vacancies at a higher substitution content to retain electric neutrality, which was confirmed by XPS analysis.

Fig. 8. Mn 2p and O 1s XPS spectra of LSMF (0.45) (a, c) and LSMF (0.6) (b, d).

Fig. 8 illustrates the Mn $2p_{3/2}$ and O $1s$ XPS spectra of LSMF (X ($X = 0.45, 0.6$)). It is observed from Fig. 8(a) and (b) that there was an asymmetrical Mn $2p_{3/2}$ peak, which could be decomposed into two components at $E_b \approx 641.6$ and 642.4 eV. The former was assigned to surface Mn $^{3+}$ species whereas the latter to surface Mn $^{4+}$ species [29]. By curve fitting, one can decompose the asymmetrical O $1s$ XPS peak into three components at $E_b \approx 528.6, 531.2$ and 532 eV, which were due to surface lattice oxygen (O_{lat}), adsorbed oxygen (O_{ads}) and hydrated oxide species (Fig. 8(c) and (d)) [30]. It can be observed from Table 3 that the surface Mn $^{4+}$ /Mn $^{3+}$ molar ratio (1.14) of LSMF (0.6) was much higher than that (0.92) of LSMF (0.45) and the O_{ads}/O_{lat} molar ratio (1.09) of LSMF (0.6) was also higher than that (0.93) of LSMF (0.45). This result indicated that the surface of LSMF (0.6) exposed more abundant surface Mn $^{4+}$ species and adsorbed oxygen species. The existence of more Mn $^{4+}$ ions increased the oxygen vacancies of an oxide material and surface oxygen vacancies is beneficial to the adsorption, activation and migration of oxygen [31], which would accelerate the formation of more adsorbed oxygen species. In addition, adsorbed oxygen species played an important role in oxidation reactions [32,33]. So, it can be concluded that the existence of more Mn $^{4+}$ ions, surface oxygen vacancies and adsorbed oxygen species contributed to a higher catalytic performance for CO oxidation on LSMF (0.6).

To evaluate the catalytic stability, on-stream reaction experiments were carried out over LSMF (0.45) and LSMF (0.6) at 250 °C (where 100% $X(CO)$ was achieved) and 500 °C (a temperature higher than the sintering temperature in the preparation of the samples) for 10 h, respectively. As shown in Fig. 9(a)

and (b), for LSMF (X ($X = 0.45, 0.6$)), only about 0.27% and 0.18% change in $X(CO)$ at 250 °C for 10 h were detected. In other words, there was no significant decrease with reaction time and 100% $X(CO)$ was indeed achieved at 250 °C on LSMF (X ($X = 0.45, 0.6$)). In addition, the variation of $X(CO)$ for both samples within 10 h at 500 °C was less than 0.025%. After reaction at 500 °C for 10 h, $X(CO)$ with the increase of reaction temperature was tested again, the results shown in Fig. 9(c). Obviously, for LSMF (0.6), $X(CO)$ under different reaction temperatures changed a little and even between 150 to 225 °C, $X(CO)$ was higher than that before reaction at 500 °C for 10 h. For LSMF (0.45), after 125 °C, it also exhibited a higher catalytic activity. By comparison, it can be concluded that the spherical porous LSMF (X ($X = 0.45, 0.6$)) samples were catalytically stable under the reaction conditions.

4. Conclusions

By the molten salt method, porous $LaMn_{0.8}Fe_{0.2}O_3$ microspheres with good crystallinity, high specific surface area and better catalytic performance for CO oxidation were obtained in two stages at 450 °C for 4 h in eutectic $NaNO_3$ - KNO_3 using hierarchical porous δ - MnO_2 microspheres assembled from interleaving thin nanosheets as the precursor template. In addition, under the conditions of $CO/O_2/Ar$ (balance) molar ratio = 1/1.25/97.75 and GHSV = 12000 h $^{-1}$, compared with the other samples prepared by the same method, the $La_{0.4}Sr_{0.6}Mn_{0.8}Fe_{0.2}O_3$ sample exhibited the best catalytic performance and stability for CO oxidation due to the existence of more Mn $^{4+}$ ions, surface oxygen vacancies and adsorbed oxygen species.

Table 3
XPS results of LSMF(X) ($X = 0.45, 0.6$).

Sample	Mn $2p$			O $1s$		O_{ads}/O_{lat}	Mn $^{4+}$ /Mn $^{3+}$
	Mn	E_b /eV	Area	$E_b^*/$ eV	Area		
LSMF (0.45)	$2p_{1/2}$	653.95	659.64	532.84 (H)	281.47	0.93	0.92
	$2p_{3/2}$	643.05	411.24	531.05 (A)	548.59		
	$2p_{3/2}$	642.02	447.72	529.63 (L)	589.67		
LSMF (0.6)	$2p_{1/2}$	653.38	890.44	533.00 (H)	303.05	1.09	1.14
	$2p_{3/2}$	642.44	889.26	531.00 (A)	1510.13		
	$2p_{3/2}$	641.45	780.45	529.25 (L)	1386.19		

* H: hydroxyl oxygen; A: surface chemical oxygen; L: lattice oxygen.

Fig. 9. Catalytic activity as a function of on-stream reaction time over LSMF (X) ($X = 0.45, 0.6$). (a) 250 °C for 10 h; (b) 500 °C for 10 h after 10 h of on-stream reaction at 250 °C; (c) Catalytic activities in CO oxidation of the fresh and used catalysts after on-stream reaction.

Graphical Abstract

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Low temperature molten salt synthesis of porous $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) microspheres with high catalytic activity for CO oxidation

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A spherical porous perovskite oxide with a better morphology and higher catalytic activity for CO was synthesized by the molten salt method at 450 °C for 4 h using hierarchical porous $\delta\text{-MnO}_2$ microspheres as template.

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低温熔盐法制备球状多孔 $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) 及其催化 CO 氧化性能

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摘要: 汽车尾气中 CO, HC, NO_x, 硫化物及其颗粒粉尘严重危害人们身体健康和大气环境, 是大气环境的主要污染源之一。目前, 尾气净化是其减排的最主要方式。汽车尾气催化剂的发展经历了几代的研究, 一直以来广泛采用 Pt, Pd 和 Rh 等贵

金属, 但因其资源匮乏, 价格昂贵, 容易被 S 和 P 中毒, 因此人们逐渐将目光投向非贵金属催化剂的研发.

钙钛矿复合氧化物因具有独特的物理化学性质以及灵活的“化学剪裁”特性而在材料研究等领域颇受青睐, 有望成为贵金属催化剂的替代品. 一般而言, 催化剂的比表面积越大, 表面活性位点越多, 其催化活性越高, 且会明显降低起燃温度. 目前, 一些制备工艺, 如水热法、共沉淀法、微乳液法和硬模板法, 虽可在一定程度上提高催化剂的比表面积, 但却存在费时、耗能及制备工艺复杂等缺点. 因此, 如何简单有效地制备出大比表面积的钙钛矿型催化剂依然是一个难题.

本文以合成的分级多孔 δ - MnO_2 微球为模板, 采用熔盐法制备出球状多孔 $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) 钙钛矿氧化物, 研究了球状多孔钙钛矿氧化物的形成过程和合适的制备温度, 以及 B 位 Fe^{3+} 掺杂量为 20% 时 A 位 Sr^{2+} 掺杂量对钙钛矿催化剂结构和催化活性的影响. 采用 X 射线粉末衍射、扫描电子显微镜、透射电子显微镜、 N_2 吸附-脱附、傅里叶红外光谱 (FT-IR) 和 X 射线能谱 (XPS) 等方法对催化剂进行了表征. 在固定床石英管反应器上评价了催化剂催化 CO 氧化活性及稳定性, 采用气相色谱联接氢火焰离子化检测器检测了产物和反应物的组成.

结果表明, 以分级多孔 δ - MnO_2 微球为模板, 采用熔盐法在 450 °C 反应 4 h 制备出的球状多孔 $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.6$) 钙钛矿氧化物具有良好的结晶性、较大的比表面积 (55.73 m^2/g) 和孔体积 (0.37 cm^3/g). 其球状多孔结构的形成可分为两个阶段: 原位形成钙钛矿相和纳片表面析出钙钛矿晶粒及钙钛矿晶粒的再生长. 另外, FT-IR 光谱表明, Fe^{3+} 和 Sr^{2+} 成功进入 A, B 位. 同时, CO 转化曲线表明, B 位 Fe^{3+} 的掺杂量为 20% 时, A 位 Sr^{2+} 的掺杂量高于 30% 时可以明显改善催化剂催化 CO 氧化活性: $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ ($0 \leq x \leq 0.3$) 的 T_{50} 和 T_{90} 分别在 180 和 198 °C 左右; 而 $\text{La}_{0.55}\text{Sr}_{0.45}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 和 $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 的 T_{50} 均低于 125 °C; $\text{La}_{0.55}\text{Sr}_{0.45}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 的 T_{90} 为 181 °C, 而 $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 却仍低于 125 °C. XPS 结果则证明, 较高的催化活性得益于 $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 表面存在较多的 Mn^{4+} 、氧空位及吸附氧. 最后, $\text{La}_{0.55}\text{Sr}_{0.45}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 和 $\text{La}_{0.4}\text{Sr}_{0.6}\text{Mn}_{0.8}\text{Fe}_{0.2}\text{O}_3$ 的稳定性测试结果表明, 采用熔盐法以 δ - MnO_2 为模板在 450 °C 焙烧 4 h 制备的多孔球状钙钛矿具有较好的催化稳定性. 虽然催化剂制备工艺简单, 周期短, 但比表面积最大只有 55.73 m^2/g , 为硬模板法的 1/2, 因此提高比表面积将是今后研究的方向.

关键词: 熔盐法; 分级多孔 δ -二氧化锰微球; 球状多孔结构; 焙烧温度; 一氧化碳氧化

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