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SBA-15表面改性及其对介孔 $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ 钙钛矿型催化剂结构和性能的影响

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摘要: 本文通过改进的水热法制备了孔径较大的有序介孔 SBA-15, 其孔径(D_p)为 10.1 nm, 并采用浓盐酸、三甲基氯硅烷(TMCS)和 3-氨丙基三乙氧基硅烷(APTES)对 SBA-15 表面进行了羟基、甲基和氨基改性处理。以嫁接不同表面官能团的 SBA-15 为模板, 合成了一系列菱方晶系钙钛矿型介孔 $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ 氧化物, 系统地研究了模板 SBA-15 的表面性能对 $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ 氧化物结构和性能的影响。X 射线衍射(XRD)图谱表明, 外表面引入 $-\text{CH}_3$, 内表面羟基化和引入 $-\text{NH}_2$ 的模板有利于合成结晶度较高的、物相单一的钙钛矿结构氧化物。小角 XRD 图谱、高分辨率透射电子显微镜(HRTEM)图像以及 N_2 吸附测试结果表明, 所制备的催化剂为介孔结构。CO 氧化的催化活性测试表明, 采用表面改性的模板合成的 $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ 氧化物表现出较高的催化活性和稳定性, 在 140 °C 时可以实现 CO 的完全转化, 连续使用 100 h 后催化剂的催化活性几乎没有下降。X 射线光电子能谱(XPS)、 H_2 程序升温还原(H_2 -TPR)和 O_2 程序升温脱附(O_2 -TPD)测试结果表明, 催化剂表面丰富的吸附氧物种, 高价态的 Co 离子, 钙钛矿结构中 Sr 在表面富集, 及优良的低温氧化还原性是催化活性提高的主要原因。

关键词: SBA-15; 表面改性; 模板法; 介孔 $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$; 低温 CO 氧化

中图分类号: O643; TQ138.1+2

Surface Modification of SBA-15 and Its Effect on the Structure and Properties of Mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$

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Abstract: Mesoporous SBA-15 with mesopore diameter up to 10.1 nm was prepared by a hydrothermal method, and was further functionalized to obtain different surface properties. Thus-prepared SBA-15 was employed as a template to synthesize rhombohedrally crystallized mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ perovskite via a nanocasting method. The surface properties of the SBA-15 were adjusted by treatment with concentrated hydrochloric acid, trimethylchlorosilane (TMCS), and 3-aminopropyltriethoxysilane (APTES). A series of characterization techniques verified that all the synthesized templates possessed ordered two-dimensional hexagonal mesoporous structure, and the surface was successfully modified with methyl and amino groups. The mesoporous perovskite structure was formed in the samples and the surface properties of SBA-15 significantly influenced the structure and properties of $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ perovskite oxides. Wide-angle X-ray diffraction patterns suggested that the modified silica templates were conducive to the formation of pure perovskite frameworks with good crystallinity. The catalysts also

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possessed mesoporous structure, as confirmed by small-angle XRD patterns, high-resolution transmission electron microscopy images, and nitrogen adsorption analysis. Moreover, the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ materials synthesized using surface-functionalized templates exhibited relatively higher catalytic activity and stability in CO oxidation. Complete CO conversion could be achieved at 140 °C using the thus-prepared $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ materials, and no significant loss in catalytic activity was observed after 100 h of on-stream reaction experiments. X-ray photoelectron spectroscopy, H_2 temperature-programmed reduction, and O_2 temperature-programmed desorption experiments revealed that the existence of Co^{4+} , Sr enrichment in the perovskite structure, and high content of adsorbed oxygen species play a critical role in the enhanced catalytic activity of the catalysts. We also proposed the possible reasons for the effect of surface properties of the silica templates on the structure and properties of the $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ nanomaterials.

Key Words: SBA-15; Surface modification; Template; Mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$; Low-temperature CO oxidation

1 Introduction

Catalytic oxidation of CO is always one of the research hotspots in the field of catalysis not only due to its extensive industrial applications, such as automobile exhaust emission control, chemical processing, CO_2 lasers, sensors, fuel cell technology, as well as air purification^{1,2}, but also because of its relative simplicity as an ideal model reaction in heterogeneous catalysis³. Recently, many researchers devoted to developing novel and highly-efficient catalysts for CO oxidation¹. Noble metal catalysts exhibit high activity for CO oxidation, but they are rare, expensive, less thermally stable and easy poisoning, which limits their applications²⁻⁵.

Perovskite complex oxides (ABO_3) were found to be the most promising alternative to noble metal catalysts in a variety of catalytic processes due to their higher thermal stability and outstanding physicochemical properties⁴. Especially, La-Co-O perovskite oxides appear to be the most active among the LaBO_3 (B is transition atom from V to Ni) perovskite series for the CO complete oxidation^{6,7}. In addition, aliovalent ion doping in A site can also influence the catalytic property of perovskite-type oxides by inducing structural modification. For example, the substitution of La^{3+} ions by Sr^{2+} ions in perovskite oxides can either increase the valence state of the B site ion or generate oxygen vacancies, leading to the improvement of oxidizing ability of catalysts^{7,8}. Unfortunately, as a catalyst, the application of perovskite oxides obtained by traditional methods is limited owing to its low surface area and catalytic activity^{4,5}.

To increase the surface area of perovskite-type catalysts, many investigators have developed new methods. For example, our group prepared 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 a surface area of $55.73 \text{ m}^2 \cdot \text{g}^{-1}$ through a low temperature molten salt approach⁹. Furthermore, some researchers dispersed perovskite catalysts on high surface area supports, e.g., mesoporous SiO_2 ¹⁰, SBA-15, MCM-41¹¹, $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ ¹², and mesoporous ZrO_2 ¹³ to enhance the relative specific surface area. Recently, a template method has sparked extensive attention due to its advantage in preparing perovskite

oxides with high surface area^{5,14}. For instance, three-dimensionally ordered macroporous (3DOM) $\text{La}_{0.6}\text{Sr}_{0.4}\text{MnO}_3$ ¹⁵ with the surface areas of $32\text{--}40 \text{ m}^2 \cdot \text{g}^{-1}$ were fabricated using the well-arrayed polymethyl methacrylate (PMMA)-templating strategy. On the other hand, many mesoporous perovskite oxides such as mesoporous LaMnO_3 ¹⁶, LaCoO_3 ^{17,18} perovskite oxides with higher surface area have been synthesized *via* the nanocasting technology by using mesoporous silica as the hard template.

However, there are few reports about the effect of surface properties of SBA-15 on mesoporous perovskite oxides *via* the template method. Abundant silanol groups on silica surface are essential for a high degree of impregnation¹⁹, for silanol groups are preserved on the silica surface in contrast to the silica removed surfactant by calcinations process¹⁴, the microwave-digested mesoporous silica has been selected to prepare mesoporous metal oxides. Amino-functionalized SBA-15 shows a high affinity for relatively heavier metal ions, such as Cu^{2+} , Zn^{2+} , Cr^{3+} , Ni^{2+} and Co^{2+} ²⁰. 3D mesoporous Cr_2O_3 ²¹ and WO_3 ²² have been successfully prepared using the amine-functionalized SBA-15 as the template. SBA-15 with the methyl groups on the external surface and amine on the internal surface is used as a template to prepare Ag nanorods with the length of tens to hundreds of nanometers, the methyl groups on the external surface suppress the growth of metal particles outside the mesochannels²³. Amination of the surface silanols of the silica results in the modification of acid-base property of the silica surface, which is beneficial to accommodate large amount of acidic species²².

Herein, the effect of surface properties of SBA-15 on mesoporous perovskite oxides prepared *via* a nanocasting route was investigated. Firstly, we prepared mesoporous SBA-15 with larger pore diameter than that achieved previously, subsequently the external surface of SBA-15 was functionalized by methyl groups, and the internal surface was modified by more hydroxyl or amino groups. The catalytic activity of mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ was evaluated by CO oxidation. In addition, a possible explanation for the effect of

surface properties on $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ perovskite oxides was proposed.

2 Experimental

2.1 Materials

Pluronic P123 (relative molecular weight is 5800, $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) and pluronic F127 were purchased from Sigma-Aldrich. Lanthanum nitrate hexahydrate ($\geq 99\%$), APTES ($\geq 99\%$), TMCS ($\geq 99\%$) were obtained from Aladdin. Ethyl silicate (AR), HCl (concentration 36%–38%), NaOH ($\geq 96\%$), citric acid monohydrate ($\geq 99.5\%$), cobalt nitrate hexahydrate ($\geq 98.5\%$), strontium nitrate ($\geq 99.5\%$), ethanol ($\geq 99.7\%$) were obtained from Sinopharm Chemical Reagent Co. Deionized water was used in the whole synthesis.

2.2 Preparation and modification of silica templates

Mesoporous silica SBA-15 was prepared following the modified version of Ref.24. The main difference was P123 and F127 together as a structure-directing agent. Typically, surfactant F127 and P123 with the molar ratio of 0.0065 were dissolved in HCl solution. Several hours later, ethyl silicate (TEOS) was added into the homogeneous solution with continuous stirring at 35 °C for additional 24 h. The molar ratio for TEOS : P123 : HCl : H_2O in the mixture was 1 : 0.017 : 6 : 167. Then the solution was transferred to a Teflon-sealed autoclave and aged statically at 110 °C for 36 h. The resulting white precipitate was collected by filtration, then washing and drying, the dry powder was marked as SBA-15-s. SBA-15 was acquired by direct calcination of SBA-15-s at 350 °C for 6 h to remove the surfactant. Otherwise, SBA-15-s was treated by TMCS before calcination, and the obtained product was denoted as $\text{CH}_3\text{-SBA-15}$, which means that the external surface of SBA-15 was modified by methyl groups. The methyl modification process was carried out according to Ref. 23. $\text{CH}_3\text{-SBA-15-OH}$ referred to $-\text{CH}_3$ groups on the outer surface and hydroxylation treatment on the inner surface to produce more $-\text{OH}$ groups. Typically, $\text{CH}_3\text{-SBA-15}$ evenly dispersed in concentrated HCl, and the mixture was stirred at RT for 8 h, and then filtered, washed with distilled water until it was neutral, dried in air and the powder was labeled as $\text{CH}_3\text{-SBA-15-OH}$. $\text{CH}_3\text{-SBA-15-OH}/\text{NH}_2$ means that the surface of $\text{CH}_3\text{-SBA-15-OH}$ was further amino functionalized, and the amino group modification process was the same as Ref.23. Prior to modification by 3-aminopropyltriethoxysilane (APTES), the $\text{CH}_3\text{-SBA-15-OH}$ was dried under vacuum at 100 °C for 12 h to remove residual water.

2.3 Synthesis of mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ perovskite

The synthesis procedure of mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ is as follows: stoichiometric amounts of lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$), cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$) were dissolved in aqueous ethanol solvent. Citric acid monohydrate, as the chelating agent, was dissolved into the nitrate solution, and the

molar ratio of the citric acid to total metal ions (La^{3+} , Co^{2+} and Sr^{2+}) was 1:1. Then the as-prepared mesoporous silica was added into the complex solution. The solution was heated under stirring constantly until it became viscous, dried in an oven. Subsequently, the dry solid composite was heated in air at a rate of 5 °C·min⁻¹ from room temperature to 300 °C and further 650 °C, and the powder was sintered at the two temperatures for 2 h, respectively. Afterwards the obtained perovskite oxides were poured into 2 mol·L⁻¹ NaOH solution and stirred at 80 °C for 6 h to remove silica template. After being washed and dried, the template-free oxides were acquired. The synthesized samples were referred to as LSC-X (X=1, 2, 3), corresponding to the different templates SBA-15, $\text{CH}_3\text{-SBA-15-OH}$ and $\text{CH}_3\text{-SBA-15-OH}/\text{NH}_2$, respectively.

2.4 Characterization

The crystal structure and composition were determined by powder X-ray diffraction (XRD) using a D/max-RB type X-ray diffractometer (Bruker AXS, Germany) with Cu K_α radiation source ($\lambda=0.15418$ nm). The crystallite size was calculated with the Scherrer equation. The morphologies as well as the corresponding selected area electron diffraction (SAED) patterns of the samples were obtained by a JEM-2100F (JEOL, Japan) high-resolution transmission electron microscope (HRTEM) at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet 6700 spectrometer (Thermo, USA) in a wavenumber range of 4000 to 400 cm⁻¹ and the samples were prepared with KBr. Hydrogen temperature programmed reduction (H_2 -TPR) experiments were carried out on a Micromeritics AutoChem II 2920 apparatus (Micromeritics, USA) with a thermal conductivity detector (TCD) under a flow rate of 50 mL·min⁻¹ (5% H_2/Ar). Approximately 50 mg of sample was pretreated with Ar at 100 °C for 2 h, prior to running the H_2 -TPR experiments, and the temperature was raised from room temperature to 850 °C at a rate of 10 °C·min⁻¹. O_2 temperature programmed desorption (O_2 -TPD) experiments were carried out using BELCAT-B-293 (BEL, Japan) analyzer. Before each experiment, 100 mg of sample was pretreated in O_2 (20 mL·min⁻¹) at 500 °C for 1 h, the temperature was raised at the rate of 10 °C·min⁻¹, then cooled down to room temperature under the same gas composition. Subsequently, O_2 was switched to He, and desorption profile recorded from room temperature to 950 °C at a heating rate of 10 °C·min⁻¹. Nitrogen adsorption/desorption measurements were performed at -196 °C using an ASAP 2020 M analyzer (Micromeritics, USA) utilizing the BET model for the calculation of specific surface areas. The pore size distribution was calculated from the adsorption isotherm curves using the Barrett-Joyner-Halenda (BJH) method. Before measurement, the samples were degassed in vacuum at 120 °C for 5 h. X-ray photoelectron spectroscopic (XPS) measurements were performed on an ESCALAB 250 Xi system (Thermo, China) equipped with Al K_α radiation source ($h\nu=1486.6$ eV) at room

temperature and under a vacuum of 10^{-7} Pa. The error of binding energy was ± 0.2 eV and the binding energy was calibrated referencing to C 1s peak ($E_b = 284.6$ eV).

2.5 Catalytic performance

The catalytic activity in oxidation of CO was examined with a continuous-flow fixed-bed quartz reactor (inner diameter is 8 mm) at a temperature range from room temperature to 180 °C. The temperature was controlled using a temperature controller connected to a thermocouple inserted in the reactor. The catalysts (approximately 100 mg) were dispersed on quartz wool and loaded into reactor; the mass ration of catalyst to quartz wool is 1:5.2% (volume fraction) CO, 3% O₂ and Ar as balance gas were fed through a mass flow controller at a total flow rate of 200 mL·min⁻¹, and the space velocity (GHSV) was 20000 h⁻¹. The outlet gas composition was determined by gas chromatograph (GC-7890 II, China) equipped with FID and TCD double detector.

3 Results and discussion

3.1 Characterization of the silica templates

The small-angle XRD spectrum in Fig.1 exhibits three characteristic diffraction peaks of two-dimensional hexagonal structure corresponding to (100), (110) and (200) diffractions^{22,23,25}. It is evident that the long-range order mesostructure is retained after hydroxylation and modification with methyl or amino, but the mesopore order of CH₃-SBA-15-OH/NH₂ decreases for the peak intensity decreases²⁶. On the contrary, the peak intensity for CH₃-SBA-15-OH increases, indicating that the order and stability of mesoporous SBA-15 increase after hydroxylation, which is in favor of dipping of precursor. Also we could see that the main diffraction peaks shift slightly to higher angle compared to the unmodified mesoporous silica template, which is owing to the shrinkage of

Fig.1 Small-angle XRD patterns of silica template.

the aperture during surface modification, indicating that the functional amino groups and silanols have been grafted into the SBA-15 pores^{22,27}.

Fig.2 shows the TEM images of all the templates. We can clearly see the parallel channels with two-dimensional hexagonal structure for each sample, suggesting that the long-range order mesostructure is reserved in CH₃-SBA-15-OH and CH₃-SBA-15-OH/NH₂ during the functionalization reaction. The results are in good agreement with the XRD analysis. Furthermore, the pore size of SBA-15 is about 10 nm as analyzed by Digital Micrographdemo software, which is consistent with the nitrogen adsorption results.

According to the IUPAC classification, the N₂ adsorption/desorption isotherms of SBA-15, CH₃-SBA-15-OH and CH₃-SBA-15-OH/NH₂ display a typical type IV isotherm with a hysteresis loop of H1(Fig.3), indicating that they possess highly ordered mesoporous structure. Apparently, CH₃-SBA-15-OH/NH₂ has a relatively low adsorption volume. In addition, all the samples show a narrow pore size

Fig.2 TEM images of SBA-15 (A, B), CH₃-SBA-15-OH (C) and CH₃-SBA-15-OH/NH₂ (D).

distribution, and the textural parameters, such as the BET surface area, the pore size and the cumulative adsorption pore volume for the synthesized samples, are summarized in Table 1. Unmodified SBA-15 has larger pore size (10.1 nm) and higher surface area ($802 \text{ m}^2 \cdot \text{g}^{-1}$). The BET surface area, pore size and the pore volume of $\text{CH}_3\text{-SBA-15-OH/NH}_2$, $\text{CH}_3\text{-SBA-15-OH}$ are smaller than those of SBA-15, further indicating that $-\text{NH}_2$ and $-\text{OH}$ are anchored onto the inner surface of SBA-15²⁷. The results are corresponding to the XRD analysis.

The successful modification of the hydroxyl, methyl group or amine group can be further demonstrated by FT-IR analysis as shown in Fig.4. For each sample, the absorption bands at 1080 , 470 and 804 cm^{-1} are assigned to asymmetric stretching, bending mode center and symmetric stretching vibrations of Si-O-Si , respectively, which confirms the existence of an SBA-15 framework^{23,25,27}. The bands at 1630 and 3432 cm^{-1} are ascribed to the bending vibration and stretching modes of $-\text{OH}$ group^{23,25,26}, respectively, and weak peaks associated with Si-OH groups stretching vibration in the range of $940\text{--}960 \text{ cm}^{-1}$ are also present. Compared with SBA-15, the peak intensity of $\text{CH}_3\text{-SBA-15-OH}$ increases at 960 , 1630 and 3413 cm^{-1} , suggesting that there are much more silanols generated on the surface of silica. In contrast, the intensity of $-\text{OH}$ group peaks decreases in $\text{CH}_3\text{-SBA-15-OH/NH}_2$, resulting from the reaction between Si-OH and APTES²³. On the modified SiO_2 samples, the absorption bands appearing in the range of $2850\text{--}3000$, 1490 and 1380 cm^{-1} are corresponding to the C-H stretching and bending vibrations^{23,25,27,28}. The N-H bending vibration around 687 cm^{-1} ²⁵⁻²⁷ and the presence of N-H stretching vibration at 1570 cm^{-1} further confirmed the incorporation of amino groups in $\text{CH}_3\text{-SBA-15-OH/NH}_2$ ²⁷.

3.2 Characterizations of mesoporous LSC-X perovskite

Wide-angle XRD pattern of the samples is shown in Fig.5A. All samples possess rhombohedral perovskite crystal structure similar to LaCoO_3 (JCPDS PDF# 48-0123 $R\bar{3}c$) and the diffraction peaks could be well indexed. One weak diffraction signal at $2\theta = 36.8^\circ$ attributable to the (311) reflection of Co_3O_4 (JCPDS PDF# 45-1003 $Fd\bar{3}m$) has been detected in the LSC-1 perovskite oxide, indicating the formation of cubic phase

Co_3O_4 in the perovskite when using unmodified SBA-15 as a template. The average sizes were estimated by Sherrer's equation $D(hkl) = 0.89\lambda/(\beta\cos\theta)$ ²⁹ for XRD peak at $2\theta = 33^\circ$, which are in the range of $16\text{--}18 \text{ nm}$ for $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ patterned by hard template SBA-15 with different surface properties, respectively. It can be clearly observed that diffraction peak of Co_3O_4 becomes weaker and even disappear in LSC-2 and LSC-3, respectively. On the contrary, diffraction peaks of main phase perovskite become much sharper, which implies the improved crystallinity of perovskite oxides¹⁷, demonstrating that surface modified SBA-15 contributes to synthesizing well crystallized pure perovskite phase by the co-nanocasting template method, which may be due to the heat released by decomposition of APTES and TMCS during calcination, leading to a better crystallization of perovskite phase.

The small-angle XRD pattern of the synthesized LSC-X samples is illustrated in Fig.5B, one weak characteristic diffraction peak corresponding to (100) crystal plane can be recorded for the sample LSC-2 and LSC-3, suggesting that some mesostructure has been obtained¹⁸. During impregnation of $\text{CH}_3\text{-SBA-15-OH}$ and $\text{CH}_3\text{-SBA-15-OH/NH}_2$, the hydrophobic external surface, the strong chelating ability of amine to metal ions citrate complex or the abundant silanol groups on the internal surface would favor the encapsulation of nitrate precursors into the mesochannels, so there are more precursors adsorbed into the channels of templates.

Fig.6(A–C) shows the TEM images of the samples LSC-X, respectively. It can be seen that a certain mesoporous structure of the replica LSC-X has been obtained, but the channel structure is not very clear, and big particles are also observed, suggesting that there are still some particles grown on the outer surface of SBA-15. This kind of mesopore can provide good mass transfer to the reactant molecules and easy accessibility to the active sites in the catalytic process, and finally improve the catalytic efficiency¹⁷. The prepared mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ has polycrystalline character according to the electron diffraction rings in the selected area electron diffraction (SAED) pattern, as shown in the inset of Fig.6A. For HRTEM image of the LSC-3 (insert in Fig.6C), the lattice fringes

Fig.3 N_2 adsorption-desorption isotherms (A) and pore size distribution curves (B) of silica template.

Fig.4 FT-IR spectra of silica template.

(a) SBA-15; (b) CH₃-SBA-15-OH; (c) CH₃-SBA-15-OH/NH₂.

corresponding to the (110) plane of orthorhombic La_{0.8}Sr_{0.2}CoO₃ perovskite are clearly visible, suggesting that perovskite oxides are well crystallized. The EDS pattern of LSC-3 (Fig.6D) shows that the atomic ratio of La : Sr : Co is close to 0.8 : 0.2 : 1. Additionally, very weak Si signal can be detected, and there was about 4% (mass fraction) Si remained after etching with NaOH, which may be due to the strong interaction between silica and rare earth elements, as was also found by others e.g. Ref. 16–18.

Nitrogen adsorption-desorption isotherms and the corresponding BJH pore size distribution curves of the mesoporous La_{0.8}Sr_{0.2}CoO₃ are shown in Fig.7. All samples correspond to type-IV isotherm with hysteresis loops appeared in the relative pressure range of 0.5–1.0, which is the feature of mesoporous materials synthesized by the hard template methods^{17,18}. The BET surface area, pore volume and pore size distribution of mesoporous LSC-X are listed in Table 1. The as-obtained mesoporous LSC-1 oxide exhibits the highest surface area (148 m²·g⁻¹). The modification of silica template leads to a decline of surface area and pore size, therefore, the surface area of corresponding perovskite oxides become lower. On the other hand, the surface area of LSC-3 is nearly 1/3 of that of corresponding template, confirming that template CH₃-SBA-15-OH/NH₂ can improve the filling efficiency of the precursor to a certain extent. In addition, all samples have

narrow pore diameter distribution with the peak located at around 7.2 nm (shown in Table 1) according to the BJH analysis.

The surface element compositions, metal oxidation states, and adsorbed oxygen species of the samples are characterized by XPS. Fig.8A shows the 2p spectra of cobalt in LSC-X perovskite. There is no shake-up satellite at 786–788 eV, suggesting the absence of Co²⁺ in the outmost layers^{30,31}. The Co 2p_{3/2} spectra of all LSC-X perovskite oxides show peaks around 780.5 eV (as listed in Table 2), which is higher than 779.8 eV assigned to Co³⁺ in perovskite oxides^{30,34}, indicating that Co⁴⁺ ions exist together with Co³⁺ ions^{31,32,35,41}. To maintain the charge balance in the samples during the substitution of Sr²⁺ for La³⁺ ions in the A sites, there are some Co⁴⁺ ions formed, which contributes to the higher catalytic activity^{7,33}. In addition, it should be noted that the binding energy of Co 2p_{3/2} in LSC-X increases with the sequence of LSC-1 < LSC-2 < LSC-3, indicating that the proportion of Co⁴⁺ ions increases with the modification of templates³¹. From Fig.8A, one can clearly observe that the asymmetrical Co 2p_{3/2} peak could be decomposed into two components at E_B ≈ 779.8 and 781.2, attributed to the surface Co³⁺ and Co⁴⁺ species³⁵, respectively. After quantitatively analyzing the Co 2p_{3/2} XPS spectra of the samples, as shown in Table 2, it can be seen that the Co⁴⁺/Co³⁺ molar ratio increases obviously from LSC-1 to LSC-3, and the LSC-3 possessed the highest surface Co⁴⁺/Co³⁺ molar ratio (1.99). Based on the XPS results (not shown), residual Si²⁺ ions were detected on the surface of LSC. It can be concluded that the interaction between SiO₂ and metal ions became stronger as the amino groups and silanol groups modified the surface of SBA-15, so there would be more Si²⁺ entered into the lattice. According to the electroneutrality principle, more Co⁴⁺ would be generated in LSC-3. At the same time, the Co 2p_{3/2} peaks of catalysts become stronger with the modification of the template, which further proves the existence of the high valence Co ions²⁹. From Table 2, it can be clearly seen that Co enrichment is obtained on the surface of La_{0.8}Sr_{0.2}CoO₃ samples, which is pronounced in LSC-3 and believed to conduce to good catalytic activity.

Fig.5 Wide-angle XRD patterns (A) and small-angle XRD patterns (B) of LSC-X.

(a) LSC-1; (b) LSC-2; (c) LSC-3.

As shown in Fig.8B, the asymmetrical O 1s spectrum of each sample could be decomposed into four components at $E_B \approx 529.2, 530.3, 531.3$ and 532.2 eV, assignable to the surface lattice oxygen O^{2-} , adsorbed oxygen (e.g. O_2^- , O_2^{2-} or O^-), hydroxyl groups or carbonate (CO_3^{2-}) species, and molecular water adsorbed on the surface respectively^{17,33,34}. Both O^- and O_2^{2-} are strongly electrophilic reactants that are very active for oxidation, especially at low temperature^{17,29,33}. The content (33.4% and 37.2% respectively) of adsorbed oxygen species in LSC-2 and LSC-3 are much higher than that (21%) in LSC-1.

In addition, the O_{ads}/O_{lat} ratio of LSC-X increases from 2.4 to 3.7 (Table 2). The existence of more Co^{4+} ions increases the oxygen vacancies of oxide materials and surface oxygen vacancies is beneficial to the adsorption, activation and mobility of oxygen³⁶, which will accelerate the formation of more adsorbed oxygen species. In addition, surface active oxygen species promote the enhancement in catalytic performance for low temperature oxidation^{4,39}.

As shown in Fig.8C, the Sr 3d peak can be fitted by two sets of Sr $3d_{5/2}$ and $3d_{3/2}$ doublets, the contributions at lower E_B

Fig.6 TEM images of LSC-1 (A), LSC-2 (B), LSC-3 (C), EDS pattern of LSC-3 (D).

Fig.7 N_2 adsorption-desorption isotherms (A) and pore size distribution curves (B) of LSC-X.

Fig.9 H₂-TPR and O₂-TPD profiles of LSC-X.

(a) LSC-1; (b) LSC-2; (c) LSC-3.

temperature, which may be associated with the higher content of adsorbed oxygen species⁵. Moreover, a small shoulder is observed around 245 °C for LSC-3, the phenomenon may be due to more high-valence cobalt ions appearing on the surface of LSC-3, leading to a relatively low reduction temperature¹⁷, which were testified by XPS results. It is evident that the LSC-3 sample possesses the lowest onset reduction temperature (358 °C) and a shoulder seam, suggesting that the sample is the most reducible⁵.

By using the curve-fitting approach, H₂ consumptions amounts of each reduction peak of the samples were calculated, and the results were summarized in Table 3. The H₂ consumptions in the low-temperature region (<450 °C) are 1.8, 1.9 and 2.1 mmol·g⁻¹, while those in the high-temperature region (>450 °C) are 3.5, 4.0 and 4.1 mmol·g⁻¹ for the LSC-1, LSC-2 and LSC-3 samples, respectively. It is apparent that the H₂ consumptions of the LSC-2 and LSC-3 are much larger than that of the LSC-1, demonstrating that the surface modified SBA-15 templates lead to an enhancement in reducibility.

O₂-TPD experiments were performed in order to investigate the surface and bulk oxygen species, as well as the mobility of oxygen for the as prepared catalysts. As illustrated in Fig.9B, the LSC-3 reveals three distinct O₂-desorption peaks. As reported in reference⁴¹, oxygen desorption below 400 °C (α -O) can be ascribed to chemisorbed oxygen species that are related to the oxygen vacancy in the surface or subsurface. Moreover, the peak at 400–600 °C (α' -O) is attributed to surface lattice oxygen species as generated from lattice defects, and the peak above 600 °C (β -O) corresponds to those oxygen species liberated mostly from the bulk of crystal structure, which is

often as an indicator of the mobility of the oxygen in the bulk⁴². The desorption temperature of α -O shifts towards lower temperature in the LSC-2 and LSC-3, and the amounts of weakly adsorbed oxygen species (α -O) increase in the following order: LSC-1 < LSC-2 < LSC-3 (Table 3), which are consistent with the XPS analysis, as shown in Table 2, the molar ratio of chemisorbed oxygen (O_{ads})/lattice oxygen (O_{lat}) for LSC-3 is 3.7, but that for LSC-1 is only 2.4. Furthermore, it is evident that LSC-3 possesses the highest α' -O desorption value, indicating that there are more defects in the LSC-3 than the others. The high oxygen desorption ability and oxygen mobility of LSC-3 are proposed due to its much higher lattice defects and oxygen vacancy, which is beneficial to the promotion of catalyst performance.

Before evaluating the catalytic activity of mesoporous LSC-X, a blank experiment only loading quartz wool in the reactor was carried out, under the conditions of 2% CO and 3% O₂ in volume fraction, Ar as balanced air, and GHSV = 20000 h⁻¹, no conversion of CO below 350 °C, and only 0.3% conversion rate were detected until 500 °C, indicating that no significant homogeneous reactions took place under the adopted reaction conditions^{5,36}. Fig.10A shows the catalytic property of mesoporous La_{0.8}Sr_{0.2}CoO₃ oxides for CO oxidation as a function of reaction temperature, and all samples exhibit excellent catalytic activity for CO oxidation at a temperature range from 120 to 180 °C. The catalytic activity increases with an order of LSC-3 > LSC-2 > LSC-1, which is in the opposite order of surface area, implying that surface area is not the determining factor for catalytic activity of catalysts. In order to better evaluate the activities of these samples, the temperatures

Table 3 The data obtained from H₂-TPR and O₂-TPD analysis.

Sample	H ₂ consumption/(mmol·g ⁻¹)			Amount of oxygen desorbed/(mmol·g ⁻¹)			
	<450 °C	≥450 °C	Total	α -O	α' -O	β -O	Total
LSC-1	1.8	3.5	5.3	0.12	0.09	1.55	1.76
LSC-2	1.9	4.0	5.9	0.15	0.17	1.57	1.89
LSC-3	2.1	4.1	6.2	0.20	0.23	1.62	2.05

Fig.10 Catalytic activities in CO oxidation of the fresh and used catalysts (A) and CO conversion as a function of on-stream reaction time over the mesoporous LSC-2 and LSC-3 (B).

($T_{50\%}$ and $T_{90\%}$, respectively) required for 50% and 90% CO conversion are employed, as summarized in Table 2. In terms of the sample LSC-3, the complete CO conversion achieved at 140 $^{\circ}\text{C}$, which is 50 $^{\circ}\text{C}$ lower than that in Ref. 18. Furthermore, $T_{90\%}$ of LSC-2 and LSC-3 (138 and 120 $^{\circ}\text{C}$, respectively) was much lower than that (252.3 $^{\circ}\text{C}$) in our previous research⁴³. It is obvious that the prepared mesoporous LSC-X samples possess much higher catalytic activity for CO oxidation. Moreover, $T_{90\%}$ of LSC-3 is 36 $^{\circ}\text{C}$ lower than that of LSC-1, indicating the surface properties of the template have some effect on the catalytic activity of mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ via a nanocasting route.

Specifically, the higher catalytic activation can be interpreted in accordance with the CO oxidation mechanism on perovskite oxides. It is reported that CO oxidation over perovskite proceeds by way of a superficial process, CO adsorbs on the perovskite oxides and reacts with surface oxygen species. The CO oxidation process on perovskite can be described as follows⁶:

It can be concluded that the surface oxygen species concentration and desorption rate of CO_2 play a critical role for CO oxidation reaction on perovskite catalysts. Meanwhile, Eq.(6) should be the rate-determining step⁶, and the desorption process of CO_2 is associated with surface cations reducibility³⁰. Obviously, the higher CO oxidation activity of LSC-3 at low temperature can be explained by better reducibility of Co ions and higher content of adsorbed oxide species on the surface, which was consistent with the XPS, H_2 -TPR and O_2 -TPD results.

In addition, the second and third catalytic cycle were performed for mesoporous LSC-2 and LSC-3 perovskite oxides after one complete catalytic test and the results are shown in Fig.10A. Interestingly, the conversion curves are much better than those of the corresponding fresh catalysts, since the

low-temperature conversion rate is found to be increased. In the second run, $T_{50\%}$ of mesoporous LSC-2 and LSC-3 samples are 108 and 105 $^{\circ}\text{C}$ respectively, which are lower than those (127 and 110 $^{\circ}\text{C}$ respectively) in fresh catalysts, the similar phenomenon was also found in our previous research shown in reference 9. One can observed that the low-temperature conversion rate in the third cycle is higher than before, but complete conversion temperature ($T_{100\%}$) becomes higher. Overall, the low-temperature catalytic activity is improved. The long-time stability experiments were conducted over LSC-2 and LSC-3 oxides for CO oxidation reaction to evaluate the catalytic stability. As shown in Fig.10B, it is conspicuous that there are no significant drops in the activity within 100 h of on-stream reaction, suggesting that the mesoporous LSC-2 and LSC-3 samples are catalytically durable.

4 Conclusions

In summary, mesoporous $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ perovskite oxides with good crystallinity are successfully fabricated by a nanocasting route from the modified SBA-15. The catalysts prepared by modified SBA-15 exhibit better structure and higher catalytic activity for CO oxidation at low-temperature. In particular, the CO complete conversion can achieve at 140 $^{\circ}\text{C}$, which is much lower than that in previous studies. The higher adsorbed species concentration, better low-temperature reducibility, the existence of Co^{4+} and good crystallinity, as well as mesoporous structure are responsible for the enhanced catalytic activity of thus-prepared perovskite catalysts. The surface properties of mesoporous silica have some effect on the structure and physicochemical properties of metal oxides, and modified mesoporous silica is expected to be applicable to synthesize other metal oxide nanomaterials with high surface area.

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