Oxidative performance and surface properties of Co-containing mixed oxides having the K$_2$NiF$_4$ structure

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Abstract: The complexed oxides Nd$_{2-x}$Sr$_x$CoO$_4$ (0.4 $\leq$ $x$ $\leq$ 1.2) and LnSrCoO$_4$ (Ln = Pr, Nd, Eu) having the K$_2$NiF$_4$ structure were synthesized by the citric-acid-complexion method. The results of XRD confirmed that the complexed oxides have the K$_2$NiF$_4$ structure. Other phases were found when $x$ = 0.4 and $x$ = 1.2. The influences of Nd, Pr, Eu on the activities of LnSrCoO$_4$ for CO oxidation and C$_3$H$_8$ oxidation were different. The oxidative activities, average crystalline size and lattice distortion of Nd$_{2-x}$Sr$_x$CoO$_4$ increased with increasing $x$ value in the oxides. When $x$ > 0.8, the lattice distortion decreased with increasing $x$. The results of O$_2$–TPD showed that amount of desorption of lattice oxygen over Nd$_{2-x}$Sr$_x$CoO$_4$ increased with $x$, however, the amount of chemodesorption of oxygen decreased. With increasing $x$, the high-temperature reduction peak in H$_2$–TPR of Nd$_{2-x}$Sr$_x$CoO$_4$ shifted to higher temperatures, however, the low-temperature reduction peak shifted to lower temperatures, which showed that the activity of the lattice oxygen and the thermal stability of Nd$_{2-x}$Sr$_x$CoO$_4$ increased with increasing $x$.

Keywords: rare earths, Co-based mixed oxides, perovskite-like, oxidation.

INTRODUCTION

CO, HC and NO$_x$ emitted from motor vehicles cause severe environmental and health problems.$^{1,2}$ In order to eliminate contamination, noble metal catalysts are widely employed at present. However, noble metal catalysts are expensive, so it is of significance to search for low cost alternatives. Perovskite-like A$_2$BO$_4$ mixed oxides having the K$_2$NiF$_4$ structure consist of alternating layers of ABO$_3$ perovskite and AO rock salt. They show high catalytic activity for the reactions involved in the after-treatment of motor vehicle exhaust gas, and have recently been studied as new materials.$^{3,4}$ At present there are many studies on LnSrCuO$_4$ and LnSrNiO$_4$, but few on LnSrCoO$_4$ (Ln = Ce, Pr, Nd, Eu). In this paper, Co-based mixed oxides LnSrCoO$_4$ and Nd$_{2-x}$Sr$_x$CoO$_4$ having the K$_2$NiF$_4$ structure were prepared by the polyglycol gel method,$^5$ and their catalytic activities for the oxidation of CO and C$_3$H$_8$ were determined.

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Catalyst preparation

Praseodymium oxide (AR), neodymium oxide (AR), europium oxide (AR), strontium nitrate (AR), cobalt nitrate (AR), polyglycol 20000 (AR) and citric acid (AR) were supplied by the Shanghai Chemical Reagent Company, China. Cerium carbonate (AR) was supplied by the Institute of Nanchang Rare Earth, China. Nitric acid (AR) and hydrochloric acid (AR) were supplied by the Jiangxi Hongdu Chemical Reagent Factory, China. Series of LnSrCoO$_4$ (Ln = Ce, Pr, Nd, Eu) and Nd$_2$Sr$_x$CoO$_4$ ($x = 0.4, 0.6, 0.8, 1.0, 1.2$) were prepared by the polyglycol gel method in the desired mole ratio. For example, when $x = 0.4$, the procedure was as follows: Nd(NO$_3$)$_3$ (0.5 mol/L, 32 mL), Sr(NO$_3$)$_2$ (0.5 mol/L, 8 mL) and 6.304 g (0.03 mol) citric acid were mixed with a solution of Co(NO$_3$)$_3$ (0.5 mol/L, 20 mL). After evaporating the solution to 40 mL at 353 K, polyglycol 20000 (20.0 g) was added under constant stirring. Stirring was continued until a viscous gel was formed. The gel was then evaporated to dryness, and the obtained precursor was calcined at 873 K for 4 h, pelletized and calcined at 1373 K for 10 h. The synthesized pellet was pulverized to ca. 0.250 - 0.177 mm.

Characterization

Powder X-ray diffraction (XRD) data were obtained using an X-ray diffractometer (type D8/ADVANCE made in Germany). The analysis conditions were as follows: target, Cu K$_\alpha$; voltage, 40 kV; current, 40 mA; scan speed, 2º min$^{-1}$. Temperature programmed desorption (TPD) experiments were carried out using an automatic Micromeritics 3000 apparatus interfaced to a data station. In each TPD experiment, the samples (0.300 g) for O$_2$–TPD were first heated from room temperature to 1123 K at a rate of 8 K min$^{-1}$ in a flow of O$_2$ (40 mL min$^{-1}$) and then cooled to room temperature. After being He-purged for 1 h, they were heated from room temperature to 1123 K at the same rate. The samples (0.300 g) for CO$_2$–TPD were first heated from room temperature to 773 K at a rate of 8 K min$^{-1}$ in a flow of He and then cooled to room temperature in a flow of CO$_2$ (40 mL min$^{-1}$). After being He-purged for 1 h, they were heated to 773 K at the same rate. Temperature programmed reduction (TPR) experiments were carried out in the same apparatus as for the TPD experiments. Since water is produced during reduction, the gases out of the reactor were passed through a cold trap before entering the thermal conductivity detector. The samples (0.100 g) were first heated to 1173 K at a rate of 20 K min$^{-1}$ in a flow of N$_2$ (99.9 %) and then cooled to room temperature. After being 10 % H$_2$/N$_2$-purged for 1 h, they were heated to 1173 K at the same rate.

Catalytic activity measurements

The catalytic tests (0.250–0.177 mm, 0.150 g catalyst) were carried out at atmospheric pressure in an automatic Micromeritics flow reactor with a reaction mixture containing CO (5.58 vol.%), O$_2$ (6.25 vol.%), N$_2$, total WHSV (10000 h$^{-1}$) for CO+$O_2$ reaction and C$_3$H$_8$ (1.35 vol.%), O$_2$ (6.75 vol.%), N$_2$, total WHSV (12000 h$^{-1}$) for C$_3$H$_8$+$O_2$ reaction. The gas composition was analysed before and after the reaction by an in-line gas chromatograph with a thermal conductivity detector (TCD) and connected with a computer integrator system. A TDX-01 column was used for CO, N$_2$ and O$_2$ and a porapak Q column for C$_3$H$_8$ and CO$_2$. The column temperature was 323 K for both columns and the TCD temperature was 348 K.

RESULTS AND DISCUSSION

Solid characteristics of catalysts

Ganguli$^6$ proposed that the formation of the K$_2$NiF$_4$ structure requires two conditions: a tolerance factor ($t = r_A/r_B$, $1.7 < t < 2.4$) and electrovalent equilibrium. The XRD patterns of the LnSrCoO$_4$ (Ln = Ce, Pr, Nd, Eu) mixed oxides showed that Pr, Nd and Eu formed K$_2$NiF$_4$-type mixed oxides, whereas, Ce formed an ABO$_2$ mixed oxide (Fig. 1A), which may be due to an imbalance of the electrovalence caused by the special stability of Ce$^{4+}$ ($4f^0$).
XRD Patterns of Nd$_{2-x}$Sr$_x$CoO$_4$ (x = 0.4, 0.6, 0.8, 1.0, 1.2) mixed oxides showed that all the Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides have an K$_2$NiF$_4$ structure (Fig. 1B). Among them, when Nd was substituted by a small amount of Sr (x = 0.4), the tolerance factor was close to 1.7, a large amount of the Nd and Co in the sample formed K$_2$NiF$_4$-type mixed oxides, while a small amount of the Nd and Co formed Nd$_2$O$_3$ and CoO. When Nd was substituted by a large amount of Sr (x = 1.2), the superfluous Sr cannot enter into an A-site because of its larger ionic radius, which resulted in the formation of SrCO$_3$ and CoO, which was confirmed by XRD.

Oxidative activities of Co-based mixed oxide catalysts

The light-off temperature $T_{50}$ and complete conversion temperature $T_{99}$ of the catalysts (reaction temperatures of 50 % and 99 % conversion, respectively) are assigned as activities. The $T_{50}$ and $T_{99}$ of CO and C$_3$H$_8$ oxidization over EuSrCoO$_4$ catalyst are higher than those of NdSrCoO$_4$ and PrSrCoO$_4$ (Table I). The influence of the three rare earths on CO oxidation was Nd > Pr > Eu.

TABLE I. Effect of the rare earth on the catalytic activity of CO and C$_3$H$_8$ oxidization over cobalt complex oxides

<table>
<thead>
<tr>
<th>Compound</th>
<th>Co oxidation</th>
<th>C$_3$H$_8$ oxidization</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{50}$/K</td>
<td>$T_{99}$/K</td>
</tr>
<tr>
<td>PrSrCoO$_4$</td>
<td>527</td>
<td>548</td>
</tr>
<tr>
<td>NdSrCoO$_4$</td>
<td>510</td>
<td>543</td>
</tr>
<tr>
<td>EuSrCoO$_4$</td>
<td>563</td>
<td>588</td>
</tr>
</tbody>
</table>

However, their influence on C$_3$H$_8$ oxidization was Pr > Nd > Eu. Thus rare earth metals have different effects on the catalytic activities for CO and C$_3$H$_8$ oxidization. The catalytic activities of NdSrCoO$_4$ and PrSrCoO$_4$ are very similar, which results from their similar ionic radius and charge. The lower catalytic activities of EuSrCoO$_4$ may result from the lanthanide contraction.
As shown in Fig. 2, the $T_{50}$ and $T_{99}$ for CO and C$_3$H$_8$ oxidization over Nd$_{2-x}$Sr$_x$CoO$_4$ decrease with increasing $x$. The oxidation of C$_3$H$_8$ over Nd$_{2-x}$Sr$_x$CoO$_4$, because of its stable molecular structure, was more difficult than that of CO.

Effects of Sr on the structure of Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides

According to the theory of powder X-ray diffraction, the average crystallite size and the lattice distortion at [104] and [110] can be calculated, respectively, by the Scherrer equation

$$L = 0.9 \frac{\lambda}{\beta \cos \theta}$$

and

$$\beta^2 \cos^2 \theta = 4 \pi^2 (\lambda/L)^2 + 32(\varepsilon^2) \sin^2 \theta$$

where $\beta$ – half width at half maximum, $\lambda = 0.154$ nm, $\theta$ – Bragg angle, $L$ – average crystallite size, $(\varepsilon^2)^{1/2}$ – lattice distortion. The calculated values are listed in Table II.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\beta_{104}$/10$^3$</th>
<th>$\beta_{110}$/10$^3$</th>
<th>$L_{104}$/nm</th>
<th>$L_{110}$/nm</th>
<th>$(\varepsilon^2)^{1/2}$/10$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd$<em>{0.8}$Sr$</em>{1.2}$CoO$_4$</td>
<td>7.99</td>
<td>4.87</td>
<td>18.06</td>
<td>29.74</td>
<td>3.42</td>
</tr>
<tr>
<td>NdSrCoO$_4$</td>
<td>8.18</td>
<td>4.96</td>
<td>17.71</td>
<td>29.16</td>
<td>3.49</td>
</tr>
<tr>
<td>Nd$<em>{1.2}$Sr$</em>{0.8}$CoO$_4$</td>
<td>8.40</td>
<td>5.12</td>
<td>17.18</td>
<td>28.29</td>
<td>3.60</td>
</tr>
<tr>
<td>Nd$<em>{1.4}$Sr$</em>{0.6}$CoO$_4$</td>
<td>7.41</td>
<td>4.51</td>
<td>19.48</td>
<td>32.08</td>
<td>3.17</td>
</tr>
<tr>
<td>Nd$<em>{1.6}$Sr$</em>{0.4}$CoO$_4$</td>
<td>6.27</td>
<td>3.82</td>
<td>23.02</td>
<td>37.91</td>
<td>2.69</td>
</tr>
</tbody>
</table>

$\beta$ – Half width at half maximum; $L$ – average crystallite size; $(\varepsilon^2)^{1/2}$ – lattice distortion

From Table II, it can be seen that Sr has an effect on the structure of Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides. When $x < 0.8$, the average crystallite size of Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides at [104] and [110] decrease with increasing $x$, but their lattice distortion increases with in-
creasing $x$. When $x > 0.8$, the changes of the average crystallite size and the lattice distortion were opposite to the charges when $x < 0.8$, the lattice distortion of Nd$_{2-x}$Sr$_x$CoO$_4$ ($x > 0.8$) is bigger than that of Nd$_{2-x}$Sr$_x$CoO$_4$ ($x < 0.8$). When $x = 0.8$, a mutation of the lattice distortion was found. It was reported that the B-site ion of A$_2$BO$_4$ mixed oxides changes with change of the A-site ion, which causes a distortion of the BO$_6$ octahedra. The activities of A$_2$BO$_4$ mixed oxides are relative to the distortion of the BO$_6$ octahedra. With increasing distortion of BO$_6$, the B–O$_I$ bond length increases, however, the B–O$_{II}$ bond length decreases ($O_I$: the oxygen on the $c$ axes of the crystal lattice, $O_{II}$ the oxygen on the $x$–$y$ plane of the crystal lattice). The increasing of the movability of oxygen ($O_I$) is favourable for the oxidation reaction.

Effects of Sr on absorbed oxygen and lattice oxygen of Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides

The surface oxygen over an oxide catalyst exists in the equilibrium: O$_2$ (adsorption) $\leftrightarrow$ O$_2^-$ (adsorption) $\leftrightarrow$ O$^-$ (surface) $\leftrightarrow$ O$^{2-}$ (surface) $\leftrightarrow$ O$^{2-}$ (lattice). The desorption temperature of O$^{2-}$ (lattice) is higher than those of chemisorbed oxygen (O$_2$ and O$_2^-$).

As shown in Fig. 3, there were two O$_2$-desorption peaks over the Nd$_{2-x}$Sr$_x$CoO$_4$ catalysts, one ($\leq 600$ K) corresponds to the description of chemisorbed oxygen and the other ($\geq 850$ K) to the desorption of lattice oxygen. The amount of chemisorbed oxygen decreased with increasing $x$, however, the amount of lattice oxygen increased. Due to the decrease of the positive charge of the A-site of Nd$_{2-x}$Sr$_x$CoO$_4$ catalysts with increasing $x$, the amount of Co$^{3+}$ (B-site) gradually decreases and, simultaneously, the amount of Co$^{3+}$ gradually increases in order to maintain the electrovalence balance. From the bond energy of adsorption and the electric charge of the atom surface (Fig. 4), it is thought that the chemisorbed oxygen should adsorb on the surface Co$^{3+}$ position or oxygen vacancy. Due to the distortion of the BO$_6$ octahedra, the Co–O$_I$ bond length is longer than that of Co–O$_{II}$. The amount of desorbed O$_I$ is connected with Co$^{3+}$, so the amount of lattice oxygen should be directly proportional to the amount of Co$^{3+}$. Generally, CO and C$_3$H$_8$ are adsorbed on Ni$^{3+}$ over Ln$_{2-x}$Sr$_x$NiO$_4$. Hence Ni$^{3+}$ is the active center and lattice oxygen is the active...
oxygen species: the chemisorbed oxygen transforms into lattice oxygen to compensate the consumed lattice oxygen.\textsuperscript{13} The oxidation mechanism over \( \text{Nd}_{2-x}\text{Sr}_x\text{CoO}_4 \) is similar to that over \( \text{Ln}_{2-x}\text{Sr}_x\text{NiO}_4 \). As the amount of \( \text{Co}^{3+} \), the desorbed amount of lattice oxygen and the catalytic activities over \( \text{Nd}_{2-x}\text{Sr}_x\text{CoO}_4 \) all simultaneously increase with increasing \( x \), \( \text{Co}^{3+} \) can be considered to be the active center and lattice oxygen the active oxygen species.\\\\Effects of \( \text{Sr} \) on the desorption of \( \text{CO}_2 \) over \( \text{Nd}_{2-x}\text{Sr}_x\text{CoO}_4 \) mixed oxides\\\\\( \text{CO}_2 \) is one of the products of \( \text{CO} \) and \( \text{C}_3\text{H}_8 \) oxidation. Form Fig. 5, the desorption temperature of \( \text{CO}_2 \) over \( \text{Nd}_{2-x}\text{Sr}_x\text{CoO}_4 \) catalysts slightly decrease with increasing \( x \), but the areas under the peaks gradually increase.\\\\Comparing with \( \text{O}_2-\text{TPD} \) (Fig. 3), the desorption temperature of \( \text{CO}_2 \) is between those of chemisorbed oxygen and lattice oxygen. The adsorption of \( \text{CO}_2 \) can affect neither the chemisorbed oxygen nor the lattice oxygen. The adsorption of \( \text{CO}_2 \) and lattice oxygen increases with increasing \( x \), so the number of centers adsorbing \( \text{CO}_2 \) and chemisorbing ox-
ygen, as well as the number of lattice oxygens change with changing $x$.

**Effects of Sr on reductive property over Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides**

The results of TPR over catalysts Nd$_{2-x}$Sr$_x$CoO$_4$ are shown in Table III. These results suggested that there are two H$_2$-reduction peaks over Nd$_{2-x}$Sr$_x$CoO$_4$ mixed oxides, namely, a low temperature peak and a high temperature peak. The temperature of the low temperature peak gradually decreased,

<table>
<thead>
<tr>
<th>X in Nd$_{2-x}$Sr$_x$CoO$_4$</th>
<th>0.4</th>
<th>0.6</th>
<th>0.8</th>
<th>1.0</th>
<th>1.2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low-temperature peak / K</td>
<td>698</td>
<td>675</td>
<td>654</td>
<td>630</td>
<td>613</td>
</tr>
<tr>
<td>High-temperature peak / K</td>
<td>936</td>
<td>967</td>
<td>985</td>
<td>1009</td>
<td>1054</td>
</tr>
</tbody>
</table>

and the temperature of the high temperature peak gradually increased with increasing $x$. As A-site Nd$^{3+}$ and Sr$^{2+}$ could not be reduced by H$_2$ in the experimental range of temperatures (400–1200 K), it must have been B-site Co ions that were reduced by H$_2$. The low temperature peak was the reduction of Co$^{3+}$, i.e.,

$$2\text{Co}^{3+} + \text{O}^{2-} + \text{H}_2 \rightarrow 2\text{Co}^{2+} + \text{H}_2\text{O}$$

whereby the Nd$_{2-x}$Sr$_x$CoO$_4$ catalysts kept their original structure. The high temperature peak was the reduction of Co$^{2+}$, i.e.,

$$\text{Co}^{2+} \rightarrow \text{Co}^0$$

whereby the K$_2$NiF$_4$–type structure was destroyed. Hence, the thermal stability of Nd$_{2-x}$Sr$_x$CoO$_4$ catalysts increased with increasing $x$.

**CONCLUSION**

Perovskite-like LnSrCoO$_4$ (Ln = Pr, Nd, Eu) and Nd$_{2-x}$Sr$_x$CoO$_4$ ($x = 0.4$, 0.6, 0.8, 1.0, 1.2) mixed oxides having the K$_2$NiF$_4$ structure were prepared by the polyglycol gel method. The rare earths have certain effects on the catalytic activity of LnSrCoO$_4$. The amount of desorbed lattice oxygen, the amount of Co$^{3+}$ and the catalytic activities of Nd$_{2-x}$Sr$_x$CoO$_4$ increased with increasing $x$. When $x = 0.8$, a lattice distortion mutation of the Nd$_{1.2}$Sr$_{0.8}$CoO$_4$ was found.
ЛАИТАО ЛЮ, ХУА ЦЗЯНГ, ХИАОМАО ЯНГ

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Синтетисани су мешовити оксиди Nd$_{2-x}$Sr$_x$CoO$_4$ ($0.4 \leq x \leq 1.2$) и LnSrCoO$_4$ (Ln = Pr, Nd, Eu) са структуром која одговара K$_2$NiF$_4$ методом комплексирања са лимунском киселином. Резултати XRD потврђују структуру K$_2$NiF$_4$. При $x = 0.4$ и 1.2 добијају се друге фазе. Утицаји Nd, Pr и Eu на активност LnSrCoO$_4$ за оксидацију CO и C$_3$H$_8$ били су различити. Оксидациона активност, просечна величина кристалита и дисторзија кристалне решетке повећавали су се са повећањем $x$. Резултати O$_2$–TPD показали су да се количина кисеоника из решетке изнад Nd$_{2-x}$Sr$_x$CoO$_4$ повећавала са повећањем $x$, док се количина хемисорбованог кисеоника смањивала. Повећањем $x$ високотемпературни редукциони максимум на H$_2$–TPR код Nd$_{2-x}$Sr$_x$CoO$_4$ померао се ка вишем температурама, док се нискотемпературни редукциони максимум померао ка нижим температурама. Ово показује да се активност кисеоника из решетке и термичка стабилност Nd$_{2-x}$Sr$_x$CoO$_4$ повећавају са повећањем $x$.


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