Preparation of La$_{0.95}$Ce$_{0.05}$CoO$_3$ with large surface area

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The perovskite-type complex oxides, La$_{0.95}$Ce$_{0.05}$CoO$_3$, have been prepared by glycine polyacrylamide sol-gel combustion method, glycine sol-gel method and solid state reaction method. These oxides have been used successfully for combustion of methane. The La$_{0.95}$Ce$_{0.05}$CoO$_3$ samples have been investigated by XRD, BET, O$_2$-TPD and H$_2$-TPR. The effect of preparation method on the structure and performance of the catalysts has been studied. La$_{0.95}$Ce$_{0.05}$CoO$_3$ prepared by glycine polyacrylamide sol-gel combustion method shows the highest catalytic activity for combustion of methane.

Keywords: Oxides, Perovskites, Catalysts, Methane combustion, Lanthanum, Cerium, Cobalt

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Perovskites have been frequently studied as substitutes for catalysts used for oxidation since perovskite-type oxides (general formula ABO$_3$) are less expensive and often thermally more stable than noble metals$^{1-6}$. However, the perovskite-type composite oxides prepared via conventional synthesis routes have relatively low specific surface areas and show low catalytic activity, and hence their commercialized applications are limited$^{7-10}$. Therefore, new methods to prepare catalytic materials with large specific surface area are of importance. Perovskite-type complex oxides with large specific surface area have recently been reported as new catalytic materials with low cost, high catalytic activity and high stability$^{11,12}$. Wu et al.$^{13}$ have reported that the thermal decomposition of citrate precursors gives perovskite-type oxides at relatively low temperatures, such as 600-700°C. The citrate process leads to perovskites with small particle size and this process is promising for the preparation of supported perovskites. The aim of the present study is to prepare La$_{0.95}$Ce$_{0.05}$CoO$_3$ perovskites with large specific surface area in order to evaluate their activity for methane combustion. The effect of the preparation method on the physico-chemical properties and the catalytic activity has also been suggested.

Experimental

The La$_{0.95}$Ce$_{0.05}$CoO$_3$ catalysts were prepared by glycine polyacrylamide sol-gel combustion method, glycine sol-gel method and solid state reaction method. All the catalyst samples were pressed and sieved to a size of 40-60 meshes for the activity evaluation of the catalytic activity.

In the glycine polyacrylamide sol-gel combustion method (GPSC), lanthanum, cerium and cobalt nitrates in the desired molar ratio were dissolved in a glycine solution at room temperature with constant stirring. The La$_{0.95}$Ce$_{0.05}$CoO$_3$ samples have been investigated by XRD, BET, O$_2$-TPD and H$_2$-TPR. The effect of preparation method on the structure and performance of the catalysts has been studied. La$_{0.95}$Ce$_{0.05}$CoO$_3$ prepared by glycine polyacrylamide sol-gel combustion method shows the highest catalytic activity for combustion of methane.

Experimental

In the glycine polyacrylamide sol-gel combustion method (GPSC), lanthanum, cerium and cobalt nitrates in the desired molar ratio were dissolved in a glycine solution at room temperature with constant stirring. At pH 6-7, acrylamide and N,N'-methylenediacrylamide (reticulating agent) were added and the resulting solution was heated at 90-95°C. Polymerization of the organic monomer was initiated by adding azo-bis-isobutyronitrile (AIBN) dissolved in ethanol and N,N,N',N'-tetramethylethylenediamide (TEMED), which acts as a radical transfer agent. A gel was formed within a few minutes due to polymerization. Then the prepared gel was transferred into a ceramic dish and placed in an oven preheated at 350°C, and the combustion reaction was carried out. With the temperature increasing at the rate of 2°C /min, the obtained precursor was calcined at 700°C or 410°C for 2h.

In the glycine sol-gel method (GS), lanthanum, cerium and cobalt nitrates were dissolved in the desired molar ratio in glycine solution at room temperature with constant stirring. The solution was evaporated to dryness and the obtained precursor was calcined at 700°C for 2h.

In the solid state reaction method (SR), lanthanum, cerium and cobalt nitrates were dissolved in the desired molar ratio in a minimum volume of deionized water. With constant stirring, the solution was evaporated to dryness and then the obtained precursor was calcined at 950°C for 4h.

In the solid state reaction method (SR), lanthanum, cerium and cobalt nitrates were dissolved in the desired molar ratio in a minimum volume of deionized water. With constant stirring, the solution was evaporated to dryness and then the obtained precursor was calcined at 950°C for 4h.

Powder X-ray diffractometer (type D-Max-3B, operated at 40 kV and 100 mA, Japan) was used to obtain data over the range 20° ≤ θ ≤ 80°, at room temperature, using Cu Ka radiation combined with
the nickel filter, at scanning rate of 0.5° min⁻¹. BET specific surface areas were measured by nitrogen adsorption-desorption at 78K using a Micromeritics ASAP 2020 instrument.

Temperature-programmed desorption of O₂ was carried out in an inhouse apparatus over 0.1 g catalyst. The samples were first heated from room temperature to 850 °C at a rate of 10 °C/min and kept at 850 °C for 1 h, then cooled to room temperature in O₂ and finally heated at a rate of 10 °C /min in He for recording the O₂-TPD spectra.

Temperature-programmed reduction (TPR) was carried out in an inhouse apparatus over 0.1 g catalyst. Before TPR experiment the samples were pretreated at 700 °C for 2 h in air and cooled to room temperature. Then the pretreated samples were heated from room temperature to 700 °C in N₂ (35 ml/min) at a rate of 10 °C/min in order to remove possible impurities. After cooling to room temperature in N₂, a gas mixture consisting of H₂ and N₂ (5:95 v/v) was introduced into the system and heated at a rate of 10 °C/min for recording the TPR spectra.

The CH₄+O₂ reactions were carried out in a flow microreactor by feeding a gas mixture of CH₄ (1.0 vol.%), O₂ (10.0 vol.%) and N₂(balanced) over 100 mg catalyst, gas hourly space velocity (GHSV 20000 h⁻¹), reaction temperature 300-700 °C. The products of the oxidation were H₂O and CO₂. The gas composition was analyzed before and after the reaction using Porapak Q columns by online gas chromatography with thermal conductor detector (TCD), connected with a computer integrator system. The activity of the catalysts was studied as rate of conversion of methane.

Results and discussion

La₀.₉₅Ce₀.₀₅CoO₃ samples was prepared by glycine polyacrylamide sol-gel combustion method, glycine sol-gel method and solide state reaction method. The XRD patterns are presented in Fig. 1. The XRD patterns of La₀.₉₅Ce₀.₀₅CoO₃ prepared by different methods show that pure perovskite crystallinity can be obtained. It is also found that the peak locations of La₀.₉₅Ce₀.₀₅CoO₃ catalysts remain intact with the introduction of Ce³⁺ (rCe³⁺=0.103 nm). This indicates completion of crystallization. The doping Ce³⁺ ions enter the crystal lattices of LaCoO₃ on site A, and replace the La³⁺ (rLa³⁺=0.1216 nm). La₀.₉₅Ce₀.₀₅CoO₃ mixed oxide prepared by solid state reaction method is a single-phase perovskite-type oxide (calcinations at 950°C for 4 h) and no uncertain phase corresponding to metal oxide was observed. However, the maximum peak of XRD patterns is intensified and the XRD line shows a small shift to higher 2θ values with respect to La₀.₉₅Ce₀.₀₅CoO₃ prepared by GPSC and GS methods ( calcination at 700 °C for 2 h).

The nitrogen isothermal sorption of the La₀.₉₅Ce₀.₀₅CoO₃ catalysts at 78K was studied. The characteristics of the isotherms exhibit dependence on the preparation method of the catalysts. The N₂ isotherms of La₀.₉₅Ce₀.₀₅CoO₃ prepared by GPSC method show hysteresis loops, which agree with a porous morphology. Such isothermal curves exhibit an intermediate profile between type B and type D, typical of a lamella structure perforated by a large number of pores. On the other hand, the isothermal curves of La₀.₉₅Ce₀.₀₅CoO₃ prepared by GS method

<table>
<thead>
<tr>
<th>Method</th>
<th>Avg. pore size (nm)</th>
<th>BET surface area (m²/g)</th>
<th>Pore vol. (cm³/g)</th>
<th>CH₄ oxidation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>T₁₀ (°C)</td>
</tr>
<tr>
<td>GPSC</td>
<td>47.27</td>
<td>32.4</td>
<td>0.21</td>
<td>367</td>
</tr>
<tr>
<td>GS</td>
<td>—</td>
<td>13.7</td>
<td>—</td>
<td>412</td>
</tr>
<tr>
<td>SR</td>
<td>—</td>
<td>2.1</td>
<td>—</td>
<td>559</td>
</tr>
</tbody>
</table>

Fig. 1—XRD patterns of La₀.₉₅Ce₀.₀₅CoO₃ catalysts. [(a) GPSC (700 °C); (b) GS; (c) SR].
show slight hysteresis loops, which agree with the presence of a few narrow pores. However, the N₂ isotherm of La₀.₉₅Ce₀.₀₅CoO₃ prepared by SR method shows no hysteresis loops, which confirms a non-porous morphology.

The BET data of the catalysts are presented in Table 1. The BET results show that the surface area of the porous samples prepared by GPSC method is much larger than that of the samples prepared by GS method and especially by the SR method. These results indicate that the introduction of polyacrylamide sol-gel in the precursors system increases BET surface area of the catalysts and inhibits the congregating process.

The O₂-TPD curves obtained over La₀.₉₅Ce₀.₀₅CoO₃ prepared by different methods show two O₂-desorption peaks (α and β). The α peak (at 390 °C) may be attributed to the chemisorbed oxygen. The oxygen chemically adsorbed on oxygen vacancies is released by reduction of Co³⁺ according to the reaction: 2Co³⁺ + O²⁻ → 2Co²⁺ + 1/2O₂. The β peak (beyond 600 °C) may be attributed to the lattice oxygen associated with the redox steps of Co ions. Comparing different preparation methods, we find that the α and β peak areas increase gradually in the order: SR<GR<GPSC. With a similar increase in the BET surface areas, the oxygen vacancies increase. Hence, the lattice oxygen, which is easily mobile, also increases in the same order, i.e., SR<GR<GPSC.

The TPR profiles of the catalysts provide useful information about the reducibility of Coⁿ⁺ species in La₀.₉₅Ce₀.₀₅CoO₃ catalysts prepared by different methods, since both La³⁺ and Ce³⁺ of the A-site are non-reducible under the conditions of H₂-TPR. As shown in Fig. 2, there are two peaks (α and β) for all catalysts, respectively, suggesting the occurrence of a multiple-step reduction. The α peak may be attributed to chemisorption oxygen and the partial reduction of Co³⁺, i.e., 2Co³⁺ + O²⁻ + H₂ → 2Co²⁺ + H₂O. The La₀.₉₅Ce₀.₀₅CoO₃ catalysts are still preserved in the perovskite-type phase structure as a whole. The temperature of α-peak reflects binding capacity between the sample and oxygen. The β peak corresponds to the reduction of Co²⁺ to Co⁰, leading to the breakdown of the perovskite-type phase. Figure 2 shows that the α and β peak temperatures of La₀.₉₅Ce₀.₀₅CoO₃ prepared by GPSC method are observed at temperature lower than those of the catalysts prepared by GS and SR method. This indicates that the activity of vacancy oxygen and lattice oxygen over La₀.₉₅Ce₀.₀₅CoO₃ prepared by GPSC method is the maximum, and the binding capacity between Co³⁺ and oxygen is less. The chemisorbed and lattice oxygens over the La₀.₉₅Ce₀.₀₅CoO₃ prepared by GPSC method move easily, which is favorable to the combustion reaction of methane.

The conversion curves of CH₄ over these prepared samples are presented in Fig. 3 and the results of oxidation of CH₄ over La₀.₉₅Ce₀.₀₅CoO₃ catalysts are summarized in Table 1 as the 10%, 50% and 90% conversion temperatures (T₁₀, T₅₀, T₉₀). By comparing T₁₀, T₅₀ and T₉ and conversion curves of CH₄, we find that the catalytic activity of the catalysts for oxidation of CH₄ improves gradually in the following order:

![Fig. 2 - H₂-TPR profiles of La₀.₉₅Ce₀.₀₅CoO₃ catalysts. [(a) GPSC; (b) GS; (c) SR].](image1)

![Fig. 3 - CH₄ conversion as a function of temperature over La₀.₉₅Ce₀.₀₅CoO₃ catalysts. [1, (■) GPSC; 2, (●) GS; 3, (▲) SR].](image2)
GPSC > GS > SR. The \( T_{10}, T_{50}, T_{9} \) values of the catalyst prepared by GPSC method are less by 45 °C, 47 °C and 25 °C respectively, as compared to the values of the \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) catalyst prepared by GS method. The higher catalytic activity of the catalysts prepared by GPSC method may be attributed to its larger surface area. The \( T_{10}, T_{50}, T_{9} \) for \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) catalyst prepared by GS method is lower as compared to those of the \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) catalyst prepared by SR method by 47 °C, 20 °C and 15 °C respectively, and the values of \( T_{10}, T_{50}, T_{9} \) obtained over \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) prepared by GPSC method are lower than those attained over \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) prepared by SR method by 193 °C, 167 °C and 140 °C respectively. The much higher catalytic activity of \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) catalyst may be attributed to its much larger surface area. Comparing the different preparation methods and different calcination temperatures, it is seen that for \( \text{La}_{0.95}\text{Ce}_{0.05}\text{CoO}_3 \) prepared by SR method (calcination temperature 950°C), GS method (700°C) and GPSC method (700°C), the surface area increases gradually as shown by the BET data. For SR method, high temperature calcination can cause agglomeration of particles and lead to lower BET surface area, which are the lowest among the samples prepared by these three methods. In the GS method, the glycine forms a gel during evaporation of the nitrate solution, leading to a uniform dispersion of metal ion complexes in solution. However, the solubility of the glycine is low. In the GPSC method, glycine, acrylamide and the organic cross linking agent are dissolved before formation of the gel, and the metal ion complexes are better separated than they are in the GS method. The metal cations are complexed by glycine and yield a stable aqueous solution, which forms a gel by radical polymerization of organic monomers that are evenly dispersed in solution. The metal ion complexes are evenly and perfectly fixed in the gel, and hence particle size of the sample is the small, and its BET surface area is the largest among these catalysts.

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References