Effect of Sr on the properties of Ce–Zr–La mixed oxides

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Abstract: Ce–Zr–La–Sr mixed oxides, with different Sr contents, were prepared by the sol–gel method. In a flow-system microreactor, the reduction properties and the oxygen storage capacity (OSC) of the Ce–Zr–La–Sr mixed oxides were investigated by a temperature programmed reduction (TPR) and a pulse technique. It was shown that the properties of the Ce–Zr–La mixed oxides depend on the Sr content and that the optimum Sr content in the Ce–Zr–La–Sr mixed oxide is 3 mol%. The Ce–Zr–La–Sr mixed oxides doped with 3 mol% Sr (Ce0.52Zr0.4La0.05Sr0.03O1.945) has the largest specific surface area and better reduction properties and oxygen storage capacity in comparison to the other investigated samples. The XRD results of the Ce–Zr–La–Sr mixed oxides showed that their X-ray diffraction patterns are well in agreement with that of fluorite-type CeO2 with Sr ions incorporated into the Ce–Zr–La mixed oxide structures. With increasing calcination temperature, the intensity of the X-ray diffraction peaks increased, but no new peaks were observed. All of these indicate that the synthesized samples had good thermal stability.

Keywords: Ce–Zr–La–Sr mixed oxides, XRD characterization, reduction properties, oxygen storage capacity.

INTRODUCTION

Automotive emissions have a serious influence on urban environments because of the rapid development of the automobile industry and the increase of automotive pollution. Automotive exhaust has become a major source of air pollution. In conventional automotive three-way catalysts, noble metals such as platinum, palladium and rhodium have hitherto been used. Especially with regard to rhodium, the relation between supply and demand tends to be tight, because the rhodium ratio in a conventional Pt/Rh catalyst is much higher than the are-mix ratio. Accordingly, the effect of promoters on catalysts for pollution control of automotive emission has been comprehensively investigated total with the aim of decreasing the amount of noble metals and enhancing their catalytic activity.

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In recent years, CeO$_2$ materials have been extensively studied because of their wide range of applications, such as a promoter in three-way catalyst for automotive exhaust control.$^{1-3}$ CeO$_2$ is present in the majority of the formulations of three-way catalysts (TWC) due to its well-known effects on their catalytic performance: (1) oxygen storage and release capacity (OSC); (2) stabilization of the noble metal dispersion; (3) stabilization of the alumina support; (4) promotion of the water gas shift reaction. However, pure CeO$_2$ is seldom used since it is known to have poor thermal stability.$^{4,5}$ Its surface area also decreases due to changes in the pore structure and in crystallite growth. Doping with other rare earth of transition metal oxides$^{6,7}$ may improve the properties of the surface area of ceria at high temperatures. However, the improvement was found to be insignificant. Recently, there has been interest in a new generation of materials for automotive exhaust control, i.e., mixed oxides containing CeO$_2$ and ZrO$_2$. It is reported that the addition of ZrO$_2$ to ceria improves the oxygen storage capacity, redox property, thermal resistance and catalytic activity at low temperatures.$^{8-10}$ Even though the introduction of CeO$_2$–ZrO$_2$ mixed oxides into TWC represented a significant breakthrough compared to the CeO$_2$-based technology, it is now recognised that undoped CeO$_2$–ZrO$_2$ mixed oxides cannot achieve sufficient thermal stability for application as fourth generation materials in TWC converters. In fact, thermal stability above 1273 K cannot be achieved by simple CeO$_2$–ZrO$_2$ mixed oxides due to their metastable nature. In principle, a TWC must show high durability, accordingly phase separation is considered an undesirable feature of the CeO$_2$–ZrO$_2$ component since it may lead to unpredictable variations in the properties of catalysts. Trivalent dopants, such as lanthana, have been added to CeO$_2$–ZrO$_2$ mixed oxides$^{15-17}$ to improve the mixed oxides.

Although CeO$_2$–ZrO$_2$ mixed oxides play an important role as catalysts in automotive pollution control, improvements are still pursued in order to enhance activity during air-to-fuel ratio fluctuations, to improve the oxidation rate during cold start operations and to obtain better thermal stability and durability of the catalysts. The aim of this work was to investigate the influence of the alkaline-earth metal Sr on the redox properties of Ce–Zr–La mixed oxides, Ce–Zr–La–Sr mixed oxides were prepared by the sol–gel technique, and effect of Sr on the Ce–Zr–La mixed oxides was determined by a structure thermal stability investigation, as well as oxygen storage capacity and reduction properties measurements.

**EXPERIMENTAL**

*Catalyst preparation*

Ce–Zr–La–Sr mixed oxides having a composition $\text{Ce}_{6.55-x}\cdot\text{Zr}_{0.4}\cdot\text{La}_{0.05}\cdot\text{Sr}_x\cdot\text{O}_{1.975-x}$, where $x = 0.001$, 0.03 and 0.06, were prepared by the sol–gel technique. Appropriate amounts of cerium nitrate, zirconium oxychloride, lanthanum nitrate and strontium nitrate were dissolved in de-ionized water to prepare the corresponding aqueous mixed solutions. The solutions were mixed with 0.1 mol/ml citric acid using a magnetic stirrer and heated at 343 K until a transparent yellow gel formed. The resulting gels were dried at 393 K for 4 h whereby loose powders resulted. These precursor powders were calcined at 1073 K and 1173 K for 4 h to obtain Ce–Zr–La–Sr mixed oxides.
Characterizations

The structure of the Ce–Zr–La–Sr mixed oxides was examined by X-ray diffraction (XRD) on a Rigaku D/MAX-A X-ray diffractometer system with CuKα radiation. The intensity data were collected at room temperature over a 2θ range of 10–80°. The specific surface areas were calculated from nitrogen adsorption isotherms at 77 K by the BET method using an automatic gas adsorption apparatus (ST-09, China).

Temperature-programmed reduction (TPR) of a catalyst was carried out in a flow-system microreactor with a thermal conductivity detector. A mixture of 10 vol % hydrogen in nitrogen was used as the reducing gas, with a gas flow rate of about 40 ml/min. Typically 100 mg of samples were used in each experiment. Before the initial TPR experiment, all the samples were pretreated by heating the sample up to 1073 K under a dynamic N2 atmosphere (40 ml/min) and maintaining this temperature for 1 h prior to each analysis. The reduction was carried out in a flow of the reducing gas using a heating rate of 10 K min⁻¹. Typically, the reduction was carried out up to 1073 K and then the sample was held at this temperature for 30 min. After the TPR, the sample was outgassed under a N2 flow at 1073 K for 30 min and cooled down approximately to 473 K, when the O2 uptake was measured by a pulse technique. Pulses of O2 (0.0706 ml) were injected into the flow of N2 passing over the sample until the breakthrough point was attained.

RESULTS AND DISCUSSION

BET Analysis

The chemical composition of the Sr-doped Ce–Zr–La mixed oxides and the corresponding specific surface areas are given in Table I. The specific surface areas of the samples calcined at the same temperature increased with increasing Sr content, and reached the maximal value for the sample with 3 mol% of Sr (Table I) in both samples (calcined at 1073 K and 1173 K). With further increase of the Sr content, the specific surface areas decreased. With increasing calcination temperature, the specific surface areas of the samples gradually decreased, which was the main cause of the phenomenon of sintering of the samples. Thus, it can be concluded that the optimal Sr content in Ce–Zr–La mixed oxides can improve the thermal stability and restrain them from sintering to a certain extent.

<table>
<thead>
<tr>
<th>Specific surface area/m² g⁻¹</th>
<th>1073 K</th>
<th>1173 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₁₀.₅₅Zr₀.₄La₀.₀₅O₁.₉₇₅</td>
<td>23.97</td>
<td>15.28</td>
</tr>
<tr>
<td>Ce₁₀.₅₄Zr₀.₄La₀.₀₅Sr₀.₀₁O₁.₉₅₅</td>
<td>23.36</td>
<td>16.52</td>
</tr>
<tr>
<td>Ce₁₀.₅₂Zr₀.₄La₀.₀₆Sr₀.₀₃O₁.₉₄₅</td>
<td>25.25</td>
<td>19.35</td>
</tr>
<tr>
<td>Ce₁₀.₄₉Zr₀.₄La₀.₀₆Sr₀.₀₆O₁.₉₁₂</td>
<td>21.88</td>
<td>15.18</td>
</tr>
</tbody>
</table>

XRD Analysis

One of the aims of this research was to explore the effect of Sr addition on the structure stability of Ce–Zr–La mixed oxides. The powder XRD patterns of calcined Ce–Zr–La–Sr mixed oxides are shown in Figs. 1 and 2. The following discussion is based on the peaks at 2θ ≈ 28.6°, 33.1°, 47.3° and 56.39° for the cubic,
fluorite type CeO$_2$ structure and at 2\(\theta\) \approx 30.2^\circ$, 34.5$^\circ$, 50.7$^\circ$ and 60.3$^\circ$ for the tetragonal ZrO$_2$. The powder X-ray diffraction patterns of Ce–Zr–La–Sr mixed oxides presented in Figs. 1 and 2 show that main peaks of the Ce–Zr–La–Sr mixed oxides lie at 2\(\theta\) values of approx 29.0$^\circ$, 33.7$^\circ$ and 57.5$^\circ$, which are close to those of pure cubic CeO$_2$. Thus, it can be concluded that with the employed synthesis method, fluorite-type solid solutions were formed. In addition, no evidence of extra peaks due to the formation of any Sr–O based crystalline phase was found in the XRD patterns of the calcined samples. However, composed to the Sr-undoped samples, the calculated lattice parameter of the Sr-doped samples became larger (Table II), and increased with the increasing Sr content. This could confirm that the Sr ions are incorporated into the Ce–Zr–La mixed oxide structures, expanding their crystal lattice.

**TABLE II. Average crystallite size and lattice parameter of Ce–Zr–La–Sr mixed oxides**

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Average particle size/nm</th>
<th>Lattice parameter/nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.55}$Zr$</em>{0.4}$La$<em>{0.05}$O$</em>{1.975}$</td>
<td>9.31</td>
<td>0.5304</td>
</tr>
<tr>
<td>Ce$<em>{0.54}$Zr$</em>{0.4}$La$<em>{0.05}$Sr$</em>{0.01}$O$_{1.955}$</td>
<td>8.76</td>
<td>0.5325</td>
</tr>
<tr>
<td>Ce$<em>{0.52}$Zr$</em>{0.4}$La$<em>{0.05}$Sr$</em>{0.03}$O$_{1.945}$</td>
<td>7.45</td>
<td>0.5335</td>
</tr>
<tr>
<td>Ce$<em>{0.49}$Zr$</em>{0.4}$La$<em>{0.05}$Sr$</em>{0.06}$O$_{1.915}$</td>
<td>8.27</td>
<td>0.5345</td>
</tr>
</tbody>
</table>

The XRD patterns of the Sr-doped Ce–Zr–La samples calcined at 1073 K for 4 h are presented in Fig. 1. The width of the XRD peaks changes with Sr content. The average crystallite sizes of the calcined samples estimated using the Scherrer equation are given in Table II. The average crystallite size depended on the amount of the alkaline-earth metal Sr in the samples prepared by the same technique. The optimal Sr content of 3 mol % favored the prevention or particle growth. The XRD patterns of the sample Ce$_{0.52}$Zr$_{0.4}$La$_{0.05}$Sr$_{0.03}$O$_{1.945}$ calcined at different temperatures (1073 K, 1173 K and 1273 K) for 4 h are shown in Fig. 2. It can be seen that
with increasing calcination temperature, the peak intensity of the samples increased and the width of all the XRD peaks decreased (i.e., the corresponding average crystallite size increased from 7.45 nm for calcination at 1073 K to 12.44 nm at 1273 K). The difference in the peak intensity may originate from the different degrees of crystallinity of the Ce–Zr–La mixed oxides. With increasing calcination temperature, an increase of the diffraction peak intensity was obvious in the XRD spectra, while no new peaks were observed. All of these findings indicate that the synthesized samples have good thermal stability.

**TPR Analysis**

The reduction temperatures of different Ce–Zr–La–Sr mixed oxides are given in Table III. The reduction temperatures of the samples are different from that of pure CeO₂ (the reduction temperature in bulk of pure CeO₂ is in excess of 1100 K¹⁸) and other metallic oxides, and a feature peak is observed at about 900 K, which is in agreement with literature data for CeO₂–ZrO₂ mixed oxides.¹⁹ The result indicate that for the employed preparation conditions, a solid reaction occurs between ceria, zirconia, lanthana and strontia, which is in agreement with the XRD characterization.

| TABLE III. TPR, OSC and OSC/ Ce results of Ce–Zr–La–Sr mixed oxides calcined at 1073 K |
|---------------------------------------------|----------------|----------------|
| TPR/K | OSC (at 47 K)/(ml/g) | OSC/Ce |
| 1073 K | 1073 K |
| Ce₀.₅₂Zr₀.₄La₀.₀₅O₁.₉₇₅ | 962 | 6.98 | 12.69 |
| Ce₀.₅₂Zr₀.₄La₀.₀₅Sr₀.₀₁O₁.₉₅₅ | 908 | 7.02 | 13.00 |
| Ce₀.₅₂Zr₀.₄La₀.₀₅Sr₀.₀₃O₁.₉₄₅ | 893 | 6.95 | 13.36 |
| Ce₀.₄₉Zr₀.₄La₀.₀₅Sr₀.₀₆O₁.₉₁₅ | 943 | 6.21 | 12.77 |

According to data give in Table III, it is obvious that the Sr content in the samples influenced the reduction temperature for TPR. With increasing Sr content in
the sample, the reduction peak of the sample first decreased and then increased. For the sample with the optimal Sr content (3 mol %), the reduction temperature was 69 K lower than for the Sr-undoped sample. The presence of Sr was found to cause the reduction peak of Ce–Zr–La mixed oxides to shift, and to favor enhancement of low temperature properties of Ce–Zr–La mixed oxides. The TPR reduction peak of all the samples were not changed by doping with different amounts of Sr, but a change in reduction temperature was observed.

**OSC Analysis**

One of the main roles of ceria in automotive exhaust catalysts is that of rapidly switching between CeO$_2$ and CeO$_{2-x}$ under lean and rich oxygen conditions, respectively. In pure ceria, this process is strongly dependent on redox phenomena of the surface. The surface area of ceria therefore has a negative impact on the capacity to rapidly store and release oxygen. With the introduction of dopants into the CeO$_2$ lattice, the main effects are as follows: (1) an increase in thermal stability; (2) an increased rate of diffusion of oxygen which positively influences the rapid exchange of oxygen, not only on the surface but in the bulk as well.

The total OSC values for the Ce–Zr–La–Sr mixed oxides are presented in Table III. The Sr content in Ce–Zr–La–Sr mixed oxides influenced the value of the OSC at 473 K, but with increasing Sr content in the sample, the total OSC of the sample did not vary significantly. However, the ratio between the OSC and the Ce content was different from that of the Sr-undoped sample, Table III, and when the Sr content was 3 mol % in the Ce–Zr–La–Sr mixed oxide, the value of OSC/Ce was the highest 13.36. It was found that Sr-doping promotes the oxygen storage capacity and improves the ability of activated oxygen movement in the bulk phase of these solid solutions. The reason is the introduction of the low valent Sr into the crystal lattice of Ce–Zr–La mixed oxides, which increases the OSC. However, when the Sr content in the samples is above the optimal content, it is obvious that the OSC of the samples decreases. It is probable that strontia itself has no oxygen storage capacity. If the Sr content in the samples was above the optimal content, the OSC of the Ce–Zr–La–Sr mixed oxides decreased.

**CONCLUSIONS**

In summary, CeO$_2$–ZrO$_2$ mixed oxides play an important role in automotive exhaust catalysts. La addition and doping with Sr improve the properties of CeO$_2$–ZrO$_2$ mixed oxides in terms of their disadvantages for practical application. In this study, it is found that the properties of Ce–Zr–La mixed oxides are influenced by the introduction of Sr, and that if the Sr content attains 3 %, the prepared Ce–Zr–La–Sr mixed oxides have better thermal stability, oxygen storage capacity and reduction ability at low temperature.
IZVOD

УТИЦАЈ Sr НА ОСОБИНЕ Ce–Zr–La МЕШАНОГ ОКSIDA

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Ce–Zr–La–Sr мешани оксиди са различитим садржајем Sr су припрегле зол-гел методом. Редукционе особине и капачитет за сторирање кисеоника Ce–Zr–La–Sr мешаног оксида су испитиване у проточном рекатору коришћењем температурског програмирања редукције и пулсене методе. Показано је да особине Ce–Zr–La мешаног оксида зависе од садржаја Sr и да оптималан садржај Sr износи 3 мол%. Ce–Zr–La–Sr мешани оксид дознан са 3 мол% Sr (Ce0.52Zr0.4La0.05Sr0.03O1.945) има највећу специфичну површину, боље редукционе особине и већи капачитет за сторирање кисеоника у поређењу са осталим узорцима. Резултати рендециске анализе Ce–Zr–La–Sr мешаног оксида су показали да њихови дифрактограми одговарају флоритном типу CeO2 са Sr јонима уграненим у структуру Ce–Zr–La мешаног оксида. Повећање температуре калцинације доводи до повећања интензитета дифракционих пикова, али нови пикови нису нађени. Све ово указује да синтетисани узорци имају добру термалну стабилност.

(Примљено 21. марта, ревизирано 14. јула 2005)

REFERENCES