Preparation of Mesoporous CuCe-Based Ternary Metal Oxide by Nano-Replication and Its Application to Decomposition of Liquid Monopropellant

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Mesoporous CuCe-based ternary metal oxides were synthesized using KIT-6 as a hard template through a nano-casting method. The mesoporous CuCe-based metal oxides were applied to the catalytic decomposition of the ammonium dinitramide-based liquid monopropellant. The decomposition onset temperature over the meso-CuCe ternary metal oxides was much lower than that over the CuCeOx catalyst prepared by conventional precipitation method. Higher activity of the meso-CuCe ternary metal oxides is attributed to higher surface area and larger pore size of the meso-CuCe ternary metal oxides than those of the conventional CuCe oxide. The highest activity of meso-CuCeZr catalyst among the meso-CuCe ternary metal oxide catalysts is likely due to the highest mesoporosity.

Keywords: Mesoporous Metal Oxide, Nano-Casting, CuCeZr, Decomposition, ADN.

1. INTRODUCTION

Hydrazine is widely used for liquid propellant in the aerospace industry.1 However, due to the toxicity of hydrazine, it is necessary to develop an eco-friendly propellant that replaces hydrazine. Ammonium dinitramide (ADN) is a very strong oxidant and a high energetic compound.2 Moreover, the decomposition of ADN does not generate halogen compounds. With these advantages, ADN-based monopropellant draws an attention as one of the green propellants.3 Unfortunately, there is a drawback in the ADN-based liquid propellant that its ignition is very difficult since it has high moisture contents. Therefore, catalysts capable of decomposing the liquid propellant at low temperature are needed. It has been reported that the copper-based catalyst prepared with sol-gel method is an effective catalyst for decomposition of ADN-based liquid monopropellant.4 Recently, a nano-replication method is attracting much attention for preparing mesoporous metal oxides.7,8

In this work, CuCe-based ternary metal oxides were prepared by a nano-replication method from a mesoporous silica template (KIT-6) with cubic Ia3d mesostructure. We have elucidated the relationship between chemico-physical properties of the mesoporous CuCe-based metal oxides and the catalytic performances in decomposition of ADN-based liquid monopropellant.

2. EXPERIMENTAL DETAILS

Mesoporous ternary metal oxides were synthesized via a nano-replication method. For an example synthesis of the mesoporous Cu0.18Ce0.8Zr0.02Ox, 0.52 g of Cu(NO)3·2.5H2O (Alridch), 1.52 g of Ce(NO)3·6H2O (Alridch), and 0.08 g of ZrOCl2·8H2O (Alridch) were dissolved in 4.0 g of deionized water to obtain a homogenous precursor solution. The solution was then impregnated into 5 g of the KIT-6 by an incipient wetness method. After drying at 80 °C for 12 h, it was calcined at 450 °C under...
air conditions for 3 h. Subsequently, the template was removed by washing twice with 2.0 M sodium hydroxide solution, and washing with distilled water and acetone several times. Finally, the materials obtained were dried at 80 °C for 12 h. This mesoporous material was denoted as meso-CuCeZr.

Powder X-ray diffraction (XRD) patterns were obtained by Rigaku X-ray diffractometer (D/MAX-2200) with a Cu Kα X-ray source. Nitrogen adsorption–desorption isotherms were collected on a Micromeritics Tristar ASAP 3020 system at liquid nitrogen temperature.

A mixture of 65 wt% of ADN, 20 wt% of methanol, 10 wt% of water, and 5 wt% of ammonia was used as an ADN-based liquid monopropellant. The catalytic decomposition reaction of ADN-based liquid monopropellant was performed in a constant volume reactor.1

3. RESULTS AND DISCUSSION

Figure 1 shows that nitrogen adsorption–desorption isotherms of KIT-6 and the mesoporous CuCe-based ternary metal oxides. The mesoporous CuCe-based ternary metal oxides exhibits typical type-IV hysteresis loop in the range of $p/p_0 = 0.6–1.0$, which is the characteristic of the mesoporous material.

The corresponding BJH pore size distribution curves of the mesoporous CuCe-based ternary metal oxides (Fig. 2) indicate that the meso-CuCeZr and meso-CuCeNi materials have mesoporous structure centered at about 14.2 nm and 12.4 nm, respectively. On the other hand, the meso-CuCeAl, meso-CuCeZn and meso-CuCeFe materials have dual porous structures centered at about 6.2–6.8 nm and 20.8–22.1 nm. The mesopore size of approximately 20.8–22.1 nm may be caused by the mesostructural transformation from the cubic $Ia3d$ mesostructure to the tetragonal $I41/a$ (or lower) mesostructures.9 It is noticeable that the BET surface area, pore volume and average pore size of mesoporous CuCe-based ternary metal oxides were much higher than those of the conventional CuCe oxide prepared by precipitation method (Table I).

Compared with the template KIT-6, however, the diffraction patterns of mesoporous CuCe-based ternary metal oxides did not show the peaks corresponding to the reflection of the $Ia3d$ structure (Fig. 3), suggesting that the ordered structure was destroyed during the nanoreplication procedure.10 The wide-angle XRD patterns have several peaks around 28.7°, 33.5°, 47.7° and 56.7°, which correspond to the fluorite structure of ceria (JCPDS 34-0394) in all the mesoporous CuCe-based ternary metal oxides.

**Table I.** Physical properties of mesoporous materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{BET}$ (m²/g)</th>
<th>$V_{tot}$ (cm³/g)</th>
<th>$D_p^*$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KIT-6</td>
<td>716</td>
<td>0.85</td>
<td>7.0</td>
</tr>
<tr>
<td>Meso-CuCeZr</td>
<td>167</td>
<td>0.41</td>
<td>14.2</td>
</tr>
<tr>
<td>Meso-CuCeAl</td>
<td>192</td>
<td>0.34</td>
<td>6.2 and 20.8</td>
</tr>
<tr>
<td>Meso-CuCeZn</td>
<td>189</td>
<td>0.36</td>
<td>6.2 and 21.2</td>
</tr>
<tr>
<td>Meso-CuCeNi</td>
<td>181</td>
<td>0.38</td>
<td>12.4</td>
</tr>
<tr>
<td>Meso-CuCeFe</td>
<td>210</td>
<td>0.37</td>
<td>6.8 and 22.1</td>
</tr>
<tr>
<td>CuCeOₓ</td>
<td>66</td>
<td>0.07</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Notes: *Pore sizes calculated by the BJH method, *prepared by precipitation method.
oxides. Any peaks concerning Cu oxide or other metal oxide materials are not observed in all the patterns, meaning that the copper and other metal are successfully incorporated into the ceria lattice, or such the species on the ceria surface are too small to give resolved XRD peaks.

Figure 4 exhibits the thermogram profiles of the thermal and catalytic decomposition of the ADN-based liquid monopropellant. In the case of the catalytic decomposition of the ADN-based monopropellant over the meso-CuCeZr catalyst, the decomposition starts at a temperature of 86.2 °C, denoted as the decomposition onset temperature \( T_{\text{dec}} \). The catalytic effect was clearly evidenced by decomposition temperature decrease, by comparison with thermal decomposition (165.5 °C).

Furthermore, it should be noted that the decomposition onset temperature (86.2–92.9 °C) over the meso-CuCe ternary metal oxides was much lower than the decomposition onset temperature (120.3 °C) over the CuCeO\(_x\) catalyst prepared by conventional precipitation method (Table II). This indicates higher activity of the meso-CuCe ternary metal oxides for the decomposition of an ADN-based monopropellant as compared to that over the CuCeO\(_x\) catalyst prepared by conventional precipitation method. More active sites could be exposed to the reactant owing to the high surface area of the meso-CuCe ternary metal oxides. Based on the same analogies, the highest activity of meso-CuCeZr catalyst among the meso-CuCe ternary metal oxide catalysts is likely due to the highest mesoporosity.

### 4. CONCLUSION

Mesoporous CuCe-based ternary metal oxides prepared by a nano-casting method exhibited much higher surface area and average pore size than those of the conventional CuCe oxide prepared by precipitation method. The decomposition onset temperature over the meso-CuCe ternary metal oxides was much lower than that over the conventional CuCeO\(_x\) catalyst. The highest activity of meso-CuCeZr catalyst in decomposition of ADN-based liquid monopropellant is likely due to the highest mesoporosity.

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References and Notes


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