Study on Catalysis of Cu-Fe Metal Composite Oxides to Thermal Decomposition Behavior of Bluestone

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ABSTRACT: Nano-CuFe$_2$O$_4$ catalysts with different Cu/Fe molar ratios (Cu$_n$Fe$_m$O$_{(n+1.5m)}$) were prepared by hydrothermal method. The thermal decomposition performance of Cu$_n$Fe$_m$O$_{(n+1.5m)}$ on CuSO$_4$ were determined with TG-DSC method to evaluate its catalytic activity and the roasted product was characterized by XRD. The results showed that Cu$_n$Fe$_m$O$_{(n+1.5m)}$ had superior catalytic properties and efficiency to CuSO$_4$ crystals in 1:1 Cu/Fe molar ratios and 4% Cu$_n$Fe$_m$O$_{(n+1.5m)}$ (in mass) contained. Under these conditions, the high and low temperature decomposition peaks of CuSO$_4$ were overlapped. The temperature and heat of decomposition were decreased by 29.5 °C and 112.1 J/g, respectively. The results were also confirmed by roasting experiments of CuSO$_4$·5H$_2$O in muffle furnace in the presence of Cu$_n$Fe$_m$O$_{(n+1.5m)}$ as catalyst at the same temperature.

KEY WORDS: Copper ferrite, Catalysis, Bluestone, Thermal decomposition.

INTRODUCTION
The application of Nano-CuFe$_2$O$_4$ shows an active work field to chemical workers [1-2]. In the field of catalysis, the oxygen-deficient spinel ferrates (MFe$_2$O$_4$$_{a,b}$) have been used in decomposition of CO$_2$ to carbon [3]. At present, the copper ferrate has been applied in the catalytic combustion of alcohol [4] and decomposition of acid dyes [5], hydrogenation of the fatty acid methyl ester in preparation of high-carbon alcohol [6], phenol hydroxylation [7], benzene hydroxylation [8], RDX thermal decomposition [9], carbon dioxide decomposition[10] and so on. In this article, the Cu$_n$Fe$_m$O$_{(n+1.5m)}$ was prepared by hydrothermal method, the catalytic thermal decomposition performance of CuSO$_4$ was also determined in detail for the first time.

EXPERIMENTAL SECTION
Apparatus and Reagents
The decomposing heat changes of CuSO$_4$ were determined by TG-DSC (Germany, STA2449C). and the roasted product was characterized by XRD (Holland, X’PertPRO). Cu(NO$_3$)$_2$, Fe(NO$_3$)$_3$, NaOH, CuSO$_4$, anhydrous alcohol and polyvinyl alcohol were of analytical grade.

Test
Cu(NO$_3$)$_2$·3H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O were dissolved in distilled water with different Cu/Fe molar ratios. Then NaOH solution (4 mol/L) was dropwise added into the mixture with a constant flow pump till pH 9–10.
the mixture was stirred for 0.5 h, filtrated and washed with distilled water to give the precursor, which was stirred with PVA in the high-pressure reactor at 320 °C, and 180-240 rpm for 3 h to give nano-Cu₄Fe₂O₄·5H₂O powders.

Catalysts Cu₄Fe₄O₈·5H₂O were marked with A, B, C and D with different Cu/Fe molar ratios 1:4, 1:2, 1:1 and 2:1, respectively. Those Cu₄Fe₄O₈·5H₂O were mixed in CuSO₄·5H₂O with a series of percents (0, 2 wt%, 3 wt%, 4 wt% and 5 wt%), whetted and mixed. The decomposition heat of those samples were determined by TG-DSC. At the same time, the sample was roasted in muffle furnace to confirm the decomposing temperature determined by TG-DSC.

RESULTS AND DISCUSSION

**Thermal decomposition performance of Cu₄Fe₄O₈·5H₂O on CuSO₄·5H₂O**

The influence of catalyst for the different Cu, Fe molar ratio

The Cu₄Fe₄O₈·5H₂O (A, B, C, D) were prepared and mixed in CuSO₄·5H₂O with 4wt%. Then the thermal analysis test were carried out on TG-DSC. The TG-DSC curve of CuSO₄·5H₂O was shown in Fig. 1, and the sample with 4 wt% Cu₄Fe₄O₈·5H₂O (C) was shown in Fig. 2.

Based on the results, it is noted that the Cu₄Fe₄O₈·5H₂O weakly effected on dehydration of CuSO₄·5H₂O, while strongly effected on the high and low temperature decomposition peak in CuSO₄ decomposition process, especially the high one.

The TG-DSC characteristics data of those samples were shown in Table 1. Due to the presence of Cu₄Fe₄O₈·5H₂O, the decomposition endothermic peaks of CuSO₄, the peak height and the apparent heat of decomposition decreased. In sample A, the low temperature decomposition peak of CuSO₄ was decreased by 12.3 °C, and the high one was decreased by 17.9 °C. The apparent heat of decomposition was decreased by 61.4 J/g. In sample B, C and D, the rate of high temperature decomposition increased obviously. The shoulder peak moved and overlapped with the low temperature decomposition peak. Compared with the high temperature decomposition peak, the low one was decreased by 25.1 °C, 29.5 °C and 27.8 °C, respectively. And the apparent heat of decomposition was decreased by 98.5 J/g, 112.1 J/g and 107.2 J/g, respectively. It indicated that the Cu₄Fe₄O₈·5H₂O not only decreased significantly the decomposition temperature of CuSO₄ but also increased the speed and depth of this process.

Contrasted four groups of data, the Cu₄Fe₄O₈·5H₂O(C) most significantly influenced the thermal decomposition of CuSO₄·5H₂O. In the catalyst, the CuO or Fe₂O₃ would be formed by excessive Cu or Fe through hydrothermal synthesis. It was noted that CuO had a “cooperative effect” with Cu₄Fe₄O₈·5H₂O and would enhance the catalysis to CuSO₄ decomposition. However, Fe₂O₃ did not have this capability. In addition, this effect will be decreased with too much CuO.

The influence of catalyst for the quality percentage

The Cu₄Fe₄O₈·5H₂O had been mixed in CuSO₄·5H₂O with different content (0, 2 wt%, 3 wt%, 4 wt% and 5 wt%). The characteristics data of those compounds was shown in Table 2.
The decomposition endothermic peak of CuSO₄, the peak height and the heat absorption decreased with the increasing content of Cu₄Fe₉O₆(2nm)·5H₂O. When the content of Cu₄Fe₉O₆(2nm)·5H₂O reached 2% and 3%, the two thermal decomposition peaks decreased by 5.7 °C and 9.4 °C and 9.6 °C, respectively. The apparent heat of decomposition was decreased by 35.4 J/g and 73.5 J/g, respectively. When the content of Cu₄Fe₉O₆(2nm)·5H₂O was increased to 4% and 5%, the two peaks were overlapped, and the peak height was getting smaller. Compared with high temperature decomposition peak, the temperature decreased by 29.5 °C and 29.8 °C, respectively. The apparent heat of decomposition were decreased by 35.4 J/g and 73.5 J/g, respectively. When the content of Cu₄Fe₉O₆(2nm)·5H₂O was increased from 4% to 5%, no change was observed in both peak and apparent heat of decomposition. The results showed that the catalysis of Cu₄Fe₉O₆(2nm)·5H₂O could release active O⁻ ion and yield the MFe₂O₄δ (δ<1) with oxygen vacancies. In the active sites of spinel ferrite Cu₄Fe₉O₆(2nm)·5H₂O, some Fe³⁺ could be deoxidized to Fe²⁺ and released active O⁻. When Fe²⁺ had strong reducibility and was not stable, it could absorb O₂ from the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O on its surface, then MFe₂O₄δ could be oxidized to MFe₂O₄ without the change of its spinel lattice structure. At the same time those O₂ could dissociate active O⁻ and take part in the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O again. Thus it formed an O⁻ circle. It was also found that the CuO

Table 1: Thermal decomposition performance of n-Cu₄Fe₉O₆(n+1.5m) with different Cu/Fe molar ratio to CuSO₄·5H₂O.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tₐ/°C</th>
<th>Tₚ/°C</th>
<th>ΔH(J/g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>726.4</td>
<td>777.4</td>
<td>-421.9</td>
</tr>
<tr>
<td>A</td>
<td>714.1</td>
<td>759.5</td>
<td>-360.5</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>D</td>
<td></td>
<td></td>
<td></td>
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</tbody>
</table>

Tₐ was the apex temperature of low temperature decomposition peak;
Tₚ was the apex temperature of high temperature decomposition peak;
ΔH was the apparent heat of decomposition.

Table 2: Thermal decomposition performance of CunFe₄mO(n+1.5m)(C) with different content to CuSO₄·H₂O.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Tₐ/°C</th>
<th>Tₚ/°C</th>
<th>ΔH(J/g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuSO₄·5H₂O</td>
<td>726.4</td>
<td>777.4</td>
<td>-421.9</td>
</tr>
<tr>
<td>2% Cu₄Fe₉O₆(2nm)(C)/CuSO₄·5H₂O</td>
<td>720.7</td>
<td>767.8</td>
<td>-386.5</td>
</tr>
<tr>
<td>3% Cu₄Fe₉O₆(2nm)(C)/CuSO₄·5H₂O</td>
<td>717.0</td>
<td>763.1</td>
<td>-348.4</td>
</tr>
<tr>
<td>4% Cu₄Fe₉O₆(2nm)(C)/CuSO₄·5H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5% Cu₄Fe₉O₆(2nm)(C)/CuSO₄·5H₂O</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The decomposition endothermic peak of CuSO₄, the peak height and the heat absorption decreased with the increasing content of Cu₄Fe₉O₆(2nm)·5H₂O. When the content of Cu₄Fe₉O₆(2nm)·5H₂O reached 2% and 3%, the two thermal decomposition peaks decreased by 5.7 °C, 9.4 °C and 9.6 °C, 14.3 °C, respectively. The apparent heat of decomposition was decreased by 35.4 J/g and 73.5 J/g, respectively. When the content of Cu₄Fe₉O₆(2nm)·5H₂O was increased to 4% and 5%, the two peaks were overlapped, and the peak height was getting smaller. Compared with high temperature decomposition peak, the temperature decreased by 29.5 °C and 29.8 °C, respectively. The apparent heat of decomposition were decreased by 35.4 J/g and 73.5 J/g, respectively. When the content of Cu₄Fe₉O₆(2nm)·5H₂O was increased from 4% to 5%, no change was observed in both peak and apparent heat of decomposition. The results showed that the catalysis of Cu₄Fe₉O₆(2nm)·5H₂O could release active O⁻ ion and yield the MFe₂O₄δ (δ<1) with oxygen vacancies. In the active sites of spinel ferrite Cu₄Fe₉O₆(2nm)·5H₂O, some Fe³⁺ could be deoxidized to Fe²⁺ and released active O⁻. When Fe²⁺ had strong reducibility and was not stable, it could absorb O₂ from the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O on its surface, then MFe₂O₄δ could be oxidized to MFe₂O₄ without the change of its spinel lattice structure. At the same time those O₂ could dissociate active O⁻ and take part in the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O again. Thus it formed an O⁻ circle. It was also found that the CuO

Roasting experiment
According to the test method, the Cu₄Fe₉O₆(2nm)(C) was mixed in the sample with 4 wt%, and then it was roasted under 750 °C for 4 h in muffle furnace. The sample was characterized by XRD (Fig.3). It showed that the CuSO₄ had been transformed into CuO completely under this condition. Therefore, this confirmed the conclusion of catalysis experiment.

Catalytic decomposition mechanism analysis of nano-CuFe₂O₄·5H₂O
The results showed that the catalysis of nano-Cu₄Fe₉O₆(2nm)·5H₂O weakly effect on dehydration of Cu₄Fe₉O₆(2nm)·5H₂O, while strongly to decompose CuSO₄ into CuO. In the catalytic decomposition process, the nano-Cu₄Fe₉O₆(2nm)·5H₂O could release active O⁻ ion (absorption), which would take part in and promote the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O. In the active sites of spinel ferrite Cu₄Fe₉O₆(2nm)·5H₂O, some Fe³⁺ could be deoxidized to Fe²⁺ and yielded the MFe₂O₄δ (δ<1) with oxygen vacancies. The MFe₂O₄δ had strong reducibility and was not stable, so it could absorb O₂ from the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O on its surface, then MFe₂O₄δ could be oxidized to MFe₂O₄ without the change of its spinel lattice structure. At the same time those O₂ could dissociate active O⁻ and take part in the decomposition of Cu₄Fe₉O₆(2nm)·5H₂O again. Thus it formed an O⁻ circle. It was also found that the CuO
in the catalyst had a “cooperative effect” with Cu₉Fe₉O₂₆₅₅m to decompose CuSO₄.

CONCLUSIONS

The Cu₉Fe₉O₂₆₅₅m weakly influence the dehydration of CuSO₄·5H₂O, but strongly on the thermal decomposition of CuSO₄. The catalytic activity of Cu₉Fe₉O₂₆₅₅m was related with its Cu/Fe molar ratios. When Cu/Fe molar ratios is 1:1, the Cu₉Fe₉O₂₆₅₅m had the highest catalysis, and the high and low temperature decomposition peaks of CuSO₄ were overlapped. The higher content of Cu₉Fe₉O₂₆₅₅m was, the stronger was its catalysis. It had highest catalytic efficiency with the 4 wt% Cu₉Fe₉O₂₆₅₅m, and the catalysis did not enhance obviously over this amount. The low temperature decomposition peak and the apparent heat of decomposition decreased by 29.5 °C and by 112.1J/g, respectively.

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