

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

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ABSTRACT: Nano-CuFe₂O₄ catalysts with different Cu/Fe molar ratios (Cu_nFe_mO_(n+1.5m)) were prepared by hydrothermal method. The thermal decomposition performance of Cu_nFe_mO_(n+1.5m) on CuSO₄ were determined with TG-DSC method to evaluate its catalytic activity and the roasted product was characterized by XRD. The results showed that Cu_nFe_mO_(n+1.5m) had superior catalytic properties and efficiency to CuSO₄ crystals in 1:1 Cu/Fe molar ratios and 4% Cu_nFe_mO_(n+1.5m) (in mass) contained. Under these conditions, the high and low temperature decomposition peaks of CuSO₄ 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 CuSO₄·5H₂O in muffle furnace in the presence of Cu_nFe_mO_(n+1.5m) as catalyst at the same temperature.

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

INTRODUCTION

The application of Nano-CuFe₂O₄ shows an active work field to chemical workers [1-2]. In the field of catalysis, the oxygen-deficient spinel ferrates (MFe₂O_{4-δ}) have been used in decomposition of CO₂ 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_nFe_mO_(n+1.5m) was prepared by hydrothermal method, the catalytic thermal decomposition performance of CuSO₄ was also determined in detail for the first time.

EXPERIMENTAL SECTION

Apparatus and Reagents

The decomposing heat changes of CuSO₄ were determined by TG-DSC (Germany, STA2449C). and the roasted product was characterized by XRD (Holland, X'PertPRO). Cu(NO₃)₂, Fe(NO₃)₃, NaOH, CuSO₄, anhydrous alcohol and polyvinyl alcohol were of analytical grade.

Test

Cu(NO₃)₂·3H₂O and Fe(NO₃)₃·9H₂O 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,

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1021-9986/11/2/33

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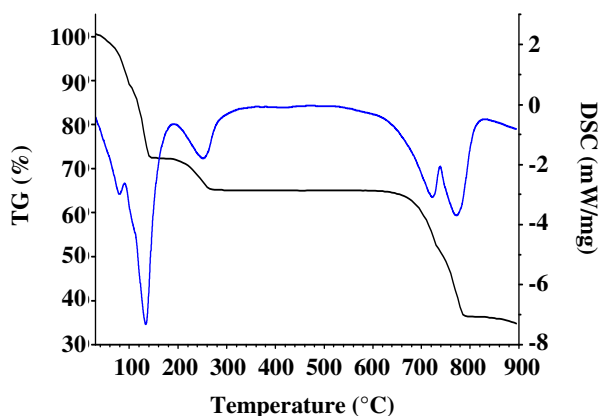


Fig. 1: TG-DSC curve of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

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- $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ powders.

Catalysts $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ 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 $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ were mixed in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ 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 $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ on $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$

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

The $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ (A, B, C, D) were prepared and mixed in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with 4wt%. Then the thermal analysis test were carried out on TG-DSC. The TG-DSC curve of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ was shown in Fig. 1, and the sample with 4 wt% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ (C) was shown in Fig. 2.

Based on the results, it is noted that the $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ weakly effected on dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, while strongly effected on the high and low temperature decomposition peak in CuSO_4 decomposition process, especially the high one.

The TG-DSC characteristics data of those samples were shown in Table 1. Due to the presence of

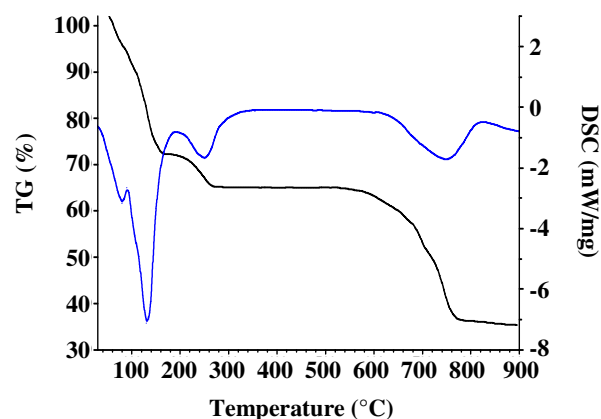


Fig. 2: TG-DSC curve of 4% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ (C)/ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.

$\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$, the decomposition endothermic peaks of CuSO_4 , the peak height and the apparent heat of decomposition decreased. In sample A, the low temperature decomposition peak of CuSO_4 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 $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ not only decreased significantly the decomposition temperature of CuSO_4 , but also increased the speed and depth of this process.

Contrasted four groups of data, the $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ (C) most significantly influenced the thermal decomposition of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$. In the catalyst, the CuO or Fe_2O_3 would be formed by excessive Cu or Fe through hydrothermal synthesis. It was noted that CuO had a "cooperative effect" with $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ and would enhance the catalysis to CuSO_4 decomposition. However, Fe_2O_3 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 $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ had been mixed in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ with different content (0, 2 wt%, 3 wt%, 4 wt% and 5 wt%). The characteristics data of those compounds was shown in Table 2.

Table 1: Thermal decomposition performance of $n\text{-Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ with different Cu/Fe molar ratio to $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$.

Samples	$T_L/^\circ\text{C}$	$T_H/^\circ\text{C}$	$\Delta H/(\text{J}\cdot\text{g}^{-1})$
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	726.4	777.4	-421.9
A	714.1	759.5	-360.5
B	The merger of the two peaks, 752.3		-323.4
C	The merger of the two peaks, 747.9		-309.8
D	The merger of the two peaks, 749.6		-314.7

T_L was the apex temperature of low temperature decomposition peak;

T_H was the apex temperature of high temperature decomposition peak;

ΔH was the apparent heat of decomposition.

Table 2: Thermal decomposition performance of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}(\text{C})$ with different content to $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$.

Samples	$T_L/^\circ\text{C}$	$T_H/^\circ\text{C}$	$\Delta H/(\text{J}\cdot\text{g}^{-1})$
$\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	726.4	777.4	-421.9
2% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}(\text{C})/\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	720.7	767.8	-386.5
3% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}(\text{C})/\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	717.0	763.1	-348.4
4% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}(\text{C})/\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	The merger of the two peaks, 747.9		-309.8
5% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}(\text{C})/\text{CuSO}_4\cdot 5\text{H}_2\text{O}$	The merger of the two peaks, 747.6		-308.1

The decomposition endothermic peak of CuSO_4 , the peak height and the heat absorption decreased with the increasing content of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$. When the content of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ 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 73.5J/g, respectively. When the content of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ 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 112.1 J/g and 113.8 J/g, respectively. When the content of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ 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 $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ was concerned with its content because more $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ would have larger effective contacted areas with CuSO_4 . The catalysis no longer enhanced if it is more than a certain amount.

Roasting experiment

According to the test method, the $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}(\text{C})$ 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 CuSO_4 had been transformed into CuO completely under this condition. Therefore, this confirmed the conclusion of catalysis experiment.

Catalytic decomposition mechanism analysis of nano- CuFe_2O_4 to $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$

The results showed that the catalysis of nano- $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ weakly effect on dehydration of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$, while strongly to decompose CuSO_4 into CuO . In the catalytic decomposition process, the nano- $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ could release active O^- ion (absorption), which would take part in and promote the decomposition of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$. In the active sites of spinel ferrite some Fe^{3+} could be deoxidized to Fe^{2+} and yielded the $\text{MFe}_2\text{O}_{4-\delta}$ ($\delta < 1$) with oxygen vacancies The $\text{MFe}_2\text{O}_{4-\delta}$ had strong reducibility and was not stable, so it could absorb O_2 from the decomposition of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ on its surface, then $\text{MFe}_2\text{O}_{4-\delta}$ could be oxidized to MFe_2O_4 without the change of its spinel lattice structure. At the same time those O_2 could dissociate active O^- and take part in the decomposition of $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ again. Thus it formed an O^- circle. It was also found that the CuO

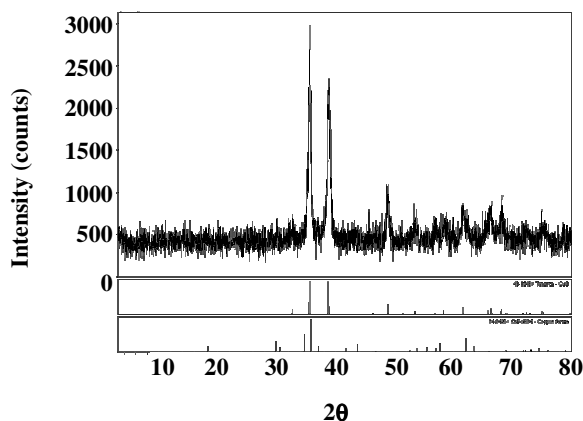


Fig. 3: XRD pattern of sample after thermal decomposition.

in the catalyst had a “cooperative effect” with $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ to decompose CuSO_4 .

CONCLUSIONS

The $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ weakly influence the dehydration of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, but strongly on the thermal decomposition of CuSO_4 . The catalytic activity of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ was related with its Cu/Fe molar ratios. When Cu/Fe molar ratios is 1:1, the $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ had the highest catalysis, and the high and low temperature decomposition peaks of CuSO_4 were overlapped. The higher content of $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$ was, the stronger was its catalysis. It had highest catalytic efficiency with the 4 wt% $\text{Cu}_n\text{Fe}_m\text{O}_{(n+1.5m)}$, and the catalysis did not enhanced 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.

Acknowledgments

The authors gratefully acknowledge the grants from the Sichuan Provincial Department of Science & Technology (No. 2008GZ0038) in support of this work.

Received : Oct. 30, 2008 ; Accepted : Sep. 15, 2010

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