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硝酸碳酰肼类含能配合物比热容的研究

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摘要：用差示扫描量热仪(DSC)测定了一定温度区间硝酸碳酰肼类配合物硝酸碳酰肼锰($Mn(CHZ)_3(NO_3)_2$)、硝酸碳酰肼钴($Co(CHZ)_3(NO_3)_2$)、硝酸碳酰肼镍($Ni(CHZ)_3(NO_3)_2$)和硝酸碳酰肼锌($Zn(CHZ)_3(NO_3)_2$)的比热容，利用 Origin7.0 软件回归出比热容随温度变化的方程式，$Ni(CHZ)_3(NO_3)_2$ 和 $Mn(CHZ)_3(NO_3)_2$ 在一些温度区间为六次函数或二、三次函数，其余大多数符合四次或五次函数，拟合时相关度最小为 0.987，标准偏差最大为 0.017。除 $Zn(CHZ)_3(NO_3)_2$ 外，其余三种硝酸碳酰肼盐配合物的比热容有较大变化，出现一个或多个峰值。对它们进行了热重和红外分析，200 ℃时仅 $Co(CHZ)_3(NO_3)_2$ 失重 8.64%，其余两种的热重曲线没有变化；红外图谱显示在不同的温度下同一物质的指纹区不同，故推测样品可能发生了晶形转变而导致比热容变化。

关键词：分析化学；差示扫描量热法；比热容；硝酸碳酰肼锰($Mn(CHZ)_3(NO_3)_2$)；硝酸碳酰肼钴($Co(CHZ)_3(NO_3)_2$)；硝酸碳酰肼镍($Ni(CHZ)_3(NO_3)_2$)；硝酸碳酰肼锌($Zn(CHZ)_3(NO_3)_2$)

中图分类号：TJ55；O642；O65 **文献标识码**：A

1 引 言

碳酰肼(CHZ)是肼的衍生物，具有很强的化学活性。是一种白色晶体，分子式为 $NH_2NHCONHNH_2$，熔点是 153 ~ 157 ℃。在含能材料领域，碳酰肼可用作含能材料的可燃剂组分，也可用作液体火药、混合炸药的组分。张同来等[1-6]人以 CHZ 为配体，以高氯酸根或硝酸根为外界阴离子，制备了一系列化合物，并对化合物的分子结构、热分解特征、爆炸性能做了研究，证明碳酰肼是一种优良的含能配体。本文测定了系列硝酸碳酰肼类含能化合物的比热容。

2 实 验

2.1 实验条件

采用美国 Perkin-Elmer 公司的 pyris-1 型差示扫描量热仪和傅立叶红外光谱仪，配备比热容数据处理软件。实验条件：流动氮气气氛，流速 20 mL·min^{-1}，升温速率为 10 K·min^{-1}，试样量 2 mg 左右，置于密封的铝钳埚进行测量。根据样品的熔点[7]，设定测试的温度区间为 50 ~ 200 ℃，开始和结束的时候等温时间 10 min。

2.2 试 样

比热容基准物：蓝宝石（直径约 3 mm，厚约 1 mm，质量为 28.56 mg）；锡粉（纯度 99.99%）：美国 PE 公司提供。

硝酸碳酰肼锰($Mn(CHZ)_3(NO_3)_2$)、硝酸碳酰肼钴($Co(CHZ)_3(NO_3)_2$)、硝酸碳酰肼镍($Ni(CHZ)_3(NO_3)_2$)和硝酸碳酰肼锌($Zn(CHZ)_3(NO_3)_2$)经过精制提纯，置于干燥器中备用。

2.3 实验方法

按实验条件分别进行空白、比热容基准物蓝宝石和样品的 DSC 测试，将得到的扫描曲线用仪器自配的比热容数据处理软件进行处理，获得在测定温度区间内样品的连续比热容[8-9]。

3 结果和讨论

实验获得样品及相应的空白和基准物的 DSC 热流曲线，以 $Mn(CHZ)_3(NO_3)_2$ 为例，其 DSC 热流曲线如图 1 所示。图 1 中实线表示样品的放大曲线。

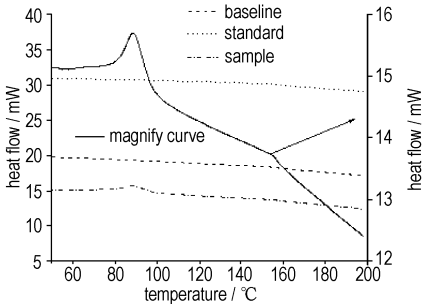

图 1 $Mn(CHZ)_3(NO_3)_2$ 的 DSC 热流曲线

Fig. 1 DSC heat flow curves of $Mn(CHZ)_3(NO_3)_2$

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由 DSC 曲线可见，除 $Zn(CHZ)_3(NO_3)_2$ 不出现峰值外，其余三种配合物的 DSC 热流曲线出现一个或多个峰值，为此对它们进行了热失重分析（见图 2）。由图 2 可见，在 200 ℃ 时 $Mn(CHZ)_3(NO_3)_2$ 和 $Ni(CHZ)_3(NO_3)_2$ 没有出现失重，$Co(CHZ)_3(NO_3)_2$ 失重 8.64%，但未出现失去结晶水的典型图谱。

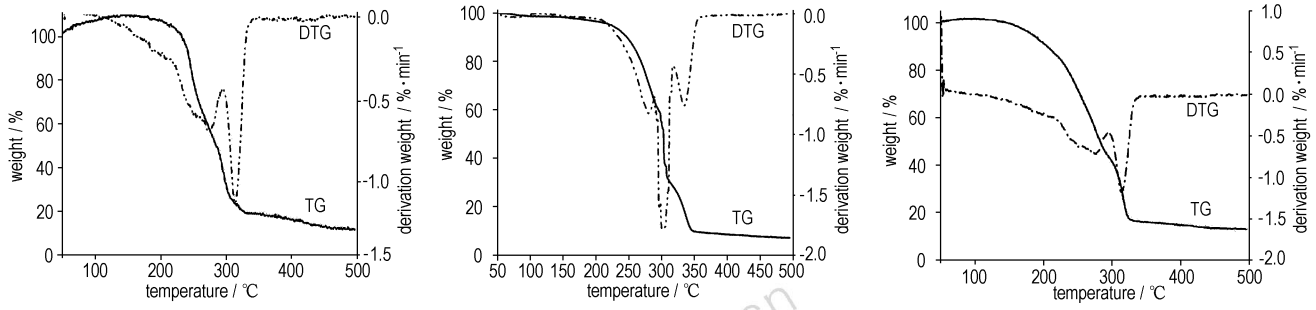
为了进一步了解比热容发生较大变化的原因，采用傅立叶红外光谱仪，对这三种化合物分别进行了室温下及加热 100 ℃ 后立即测试。仍以 $Mn(CHZ)_3(NO_3)_2$ 为例，其红外光谱如图 3 所示。从测试结果可以看出样品的红外光谱发生了较大的变化，变化主要产生在指纹区。$Mn(CHZ)_3(NO_3)_2$ 在 1383 cm^{-1} 处峰的强度变化很大。$Co(CHZ)_3(NO_3)_2$ 在 1361 cm^{-1} 处的峰强度变化很大，且出峰位置有一定偏移。由此推断三种化合物可能具有多种晶形，加热到一定温度时，晶形转变，吸收热量，比热容发生变化。

采用测试七次取平均值的方法，计算 50 ~ 140 ℃ 温度区间 $Co(CHZ)_3(NO_3)_2$ 的连续比热容以及其余样品在 50 ~ 200 ℃ 的连续比热容，其结果见图 4。

利用 Origin7.0 对所得到的比热容曲线进行拟合，获得了 4 种配合物的比热容随温度变化的方程式，结果见表 1，其中相关系数最小值为 0.987，标准偏差最大值为 0.017。它们大多符合四次或五次函数，$Ni(CHZ)_3(NO_3)_2$ 和 $Mn(CHZ)_3(NO_3)_2$ 在一些温度区间为六次或二、三次函数。

4　结　论

用 DSC 测定了 $Mn(CHZ)_3(NO_3)_2$、$Ni(CHZ)_3(NO_3)_2$ 和 $Zn(CHZ)_3(NO_3)_2$ 在温度区间为 50 ~ 200 ℃ 的连续比热容，以及 $Co(CHZ)_3(NO_3)_2$ 在 50 ~ 140 ℃ 的连续比热容，拟合了比热容随温度变化的方程式，它们大多数符合四次或五次函数，仅 $Ni(CHZ)_3(NO_3)_2$ 和 $Mn(CHZ)_3(NO_3)_2$ 在一些温度区间为六次函数或二、三次函数。用 TG、FTIR 分析了 $Mn(CHZ)_3(NO_3)_2$、$Ni(CHZ)_3(NO_3)_2$ 和 $Co(CHZ)_3(NO_3)_2$ 比热容变化较大的原因，在 200 ℃ 时，$Mn(CHZ)_3(NO_3)_2$ 和 $Ni(CHZ)_3(NO_3)_2$ 没有出现失重，$Co(CHZ)_3(NO_3)_2$ 在失重 8.64%，但未出现失去结晶水的典型图谱。加热后它们的红外光谱发生了较大的变化，推测样品可能发生了晶形转变。



(a) $Mn(CHZ)_3(NO_3)_2$　(b) $Ni(CHZ)_3(NO_3)_2$　(c) $Co(CHZ)_3(NO_3)_2$

图 2　样品的 TG-DTG 曲线

Fig. 2　TG-DTG curves of samples

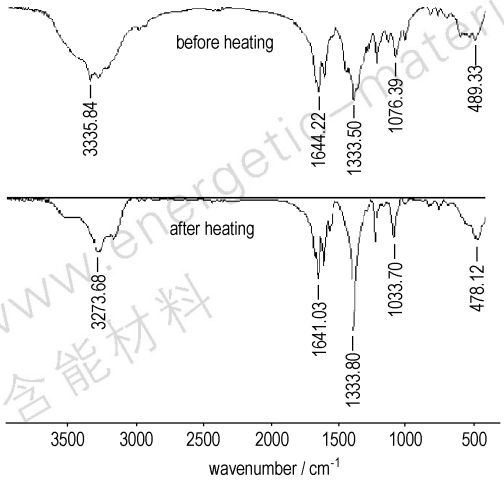


图 3　加热前后 $Mn(CHZ)_3(NO_3)_2$ 的红外光谱图

Fig. 3　FTIR spectra of $Mn(CHZ)_3(NO_3)_2$ before and after heating

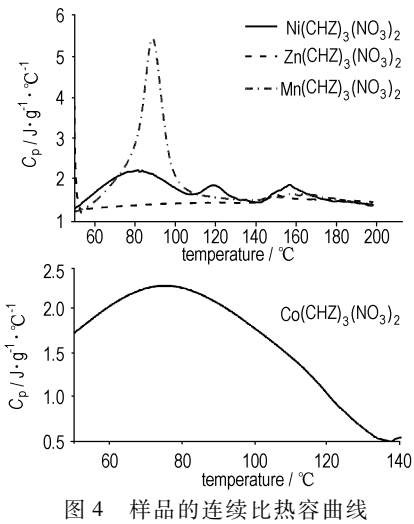


图 4　样品的连续比热容曲线

Fig. 4　Continuous curves of specific heat capacity of samples

表 1 样品的比热容方程

Table 1 Equations of specific heat capacity of samples

sample	temperature/℃	equation	*R*	SD
$Mn(CHZ)_3(NO_3)_2$	50.1 ~ 88.7	$141.182-8.895\ T+0.210\ T^2-0.002\ T^3+8.543\times10^{-6}\ T^4$	0.997	0.059
	88.7 ~ 198.6	$1962.846-81.812\ T+1.410\ T^2-0.013\ T^3+6.523\times10^{-5}\ T^4-1.751\times10^{-7}\ T^5+1.941\times10^{-10}\ T^6$	0.990	0.072
$Ni(CHZ)_3(NO_3)_2$	50.0 ~ 110.2	$20.182-1.166\ T+0.025\ T^2-2.279\times10^{-4}\ T^3+7.261\times10^{-7}\ T^4$	0.999	0.010
	110.2 ~ 141.9	$198591.102-9411.728\ T+185.469\ T^2-1.945\ T^3+0.011\ T^4-3.590\times10^{-5}\ T^5+4.680\times10^{-8}\ T^6$	0.998	0.006
	141.9 ~ 156.8	$-13.731+0.176\ T-4.873\times10^{-4}\ T^2$	0.995	0.010
	156.8 ~ 198.5	$72.629-1.129\ T+0.006\ T^2-1.063\times10^{-5}\ T^3$	0.997	0.007
$Co(CHZ)_3(NO_3)_2$	50.1 ~ 137.8	$-2.215+0.096\ T+5.546\times10^{-5}\ T^2-1.074\times10^{-5}\ T^3+4.563\times10^{-8}\ T^4$	0.999	0.017
$Zn(CHZ)_3(NO_3)_2$	56.9 ~ 150.3	$-7.472+0.482\ T-0.011\ T^2+1.128\times10^{-4}\ T^3-5.956\times10^{-7}\ T^4+1.231\times10^{-9}\ T^5$	0.990	0.006
	150.3 ~ 195.4	$2459.299-70.081\ T+0.799\ T^2-0.005\ T^3+1.292\times10^{-5}\ T^4-1.469\times10^{-8}\ T^5$	0.996	0.002

Note: *R* is relative coefficient, SD is standard deviation.

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Electrostatic Spark Sensitivity of Single Base Oblate Propellant with Micropores

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Abstract: The oblate propellant with micropores(MPOP) was prepared by chemical foamed process, and the effects of the materials and inner-structure on its electrostatic spark sensitivity were studied by adjusting the distance of discharging and the way of loading. Results show that the lower the bulk density of these oblate propellants is, the higher electrostatic spark sensitivity is. And the smaller the grain diameter of the oblate propellants is, the higher its electrostatic spark sensitivity is. The electrostatic spark sensitivity of MPOP with the bulk density not more than 0.3 $g \cdot cm^{-3}$ is apparently higher than nitrocellulose. It is feasible to test the electrostatic spark sensitivity of low-density materials with micropores using this improved method.

Key Words: physical chemistry; oblate propellant; micropore; safety behavior; electrostatic spark sensitivity

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Specific Heat Capacity of Carbohydrazide Nitric Acid Energetic Coordination Compounds

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Abstract: The specific heat capacity of four carbohydrazide nitrate energetic coordination compounds $[M(CHZ)_3](NO_3)_2$, (M = Mn, Co, Zn, Ni) were determined by differential scanning calorimeter (DSC) under a temperature range, and regression equations for the specific heat capacity changing with temperature were obtained by Origin 7.0. The equations of $Ni(CHZ)_3(NO_3)_2$ and $Mn(CHZ)_3(NO_3)_2$ are functions of sixth degree, second degree and third degree in some range of temperature, equations of the others mostly are functions of fourth degree or fifth degree, where the relative coefficient square is more than 0.987, and standard deviation is smaller than 0.017. Except $Zn(CHZ)_3(NO_3)_2$, the specific heat capacity of the compounds changes more, and one or more peaks appear in the curves of the specific heat capacity. TG and FTIR were carried through. At 200 ℃, only $Co(CHZ)_3(NO_3)_2$ loses 8.64% of its mass. As FTIR spectra are not same at different temperature, it is possible that the crystal transformation results in the change of the specific heat capacity.

Key words: analytical chemistry; differential scanning calorimeter; specific heat capacity; $Mn(CHZ)_3(NO_3)_2$; $Co(CHZ)_3(NO_3)_2$; $Ni(CHZ)_3(NO_3)_2$; $Zn(CHZ)_3(NO_3)_2$