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RESEARCH PAPER

Thermal Decomposition Mechanisms of a Three-dimensional Framework Coordination Polymer $[Cu(HCOO)_2(H_2O)_2]_\infty$

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Abstract: The crystal of $[Cu(HCOO)_2(H_2O)_2]_\infty$ (polymer **1**) has been synthesized and cultured using the hydrothermal method. The thermal decomposition mechanisms and the associated kinetics of polymer **1** have been investigated based on the TG-DTG and DSC analyses. The most probable kinetic model function of the endothermic process was suggested by comparison of the kinetic parameters obtained from the analysis of the DSC curves by Kissinger's, Ozawa's, integral, and differential methods. The crystal of polymer **1** was characterized by X-ray single crystal diffraction, elemental analysis, and FTIR spectroscopy techniques. The coordination polymer crystallizes in monoclinic system, $P2_1/c$ space group with crystal parameters of a=0.8533(2) nm, b=0.7151(2) nm, c=0.9463(2) nm, β=96.94(0)º, V=0.5732(2) nm^3, Z=4, and D_c=2.197 g·cm^{-3}. In the coordination polymer, with the formates as space linkers, two types of copper centers are joined together to form three-dimensional frameworks.

Key Words: Coordination polymer; Thermal decomposition; Nonisothermal kinetics; Formic acid; Crystal structure

Coordination polymers with novel structures that were obtained using carboxylic acids as ligands have been widely studied in the past decades because of their potential uses in magnetic materials, optical materials, gas storage, and so on[1−7]. Among all the carboxylic acids, besides aromatic carboxylic acids, acyclic carboxylic acids such as formic acid have also been used by many researchers in the preparation of microporous materials[8−14]. For example, simple metal formates with unusual structures have been synthesized under hydrothermal, solvothermal, or other conditions: $Mn(HCOO)_2 \cdot 1/3(C_4H_8O_2)$ exhibits accessible zigzag open channels in three-dimensional, charge-neutral network; Manganese(III) formate can trap carbon dioxide, formic acid, and water molecules in the three-dimensional frameworks; Iron(II) formate, a mesoporous magnet, shows an open framework structure with formic acid molecules occupying channels; $Cu(HCOO)_2 \cdot 4H_2O$ exhibits two-dimensional copper formate layers that are separated by water molecules; $Cu(HCOO)_2L$ (L=pyrazine, 4,4'-bipyridine) uses the formate anion as a building block to form three-dimensional frameworks[12−14].

Thermal analyses DSC and TG-DTG have been used to a lesser extent to study the above-mentioned coordination polymers to predict their thermal decomposition mechanisms and to determine the kinetic equations of the reactions[15−17]. In these experiments, DSC analyses of polymer **1** under static air condition and in a flowing gas have been carried out to determine the most probable model function of the dehydration reaction. The TG-DTG analysis in a flowing gas and FTIR spectra were used to predict the thermal decomposition mechanisms of polymer **1**. The crystal of the coordination polymer **1** was cultured using the hydrothermal method and was characterized using the X-ray single-crystal diffractometer. In the obtained coordination polymer **1**, formates act as space linkers to link together two types of copper centers: the bridging formates link Cu(1) centers with Cu(2) centers to form one-dimensional chains, and by means of this one-dimensional chains and the other four bridging formates of Cu(1), Cu(1) and Cu(2) atoms are bridged together to form three-dimensional frameworks.

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1 Experimental

1.1 Synthesis

A mixture of $Cu(NO_3)_2{\cdot}3H_2O$ (AR, 0.2416 g, 1 mmol), formic acid (AR, 1 mL), and distilled water (5 mL) was adjusted to pH≈6 using 1 mol·L^{-1} NaOH (AR) and then transferred and sealed in a 25-mL Teflon-lined stainless steel container. The container was heated from room temperature to 373 K at 0.5 K·min^{-1} and was held at 373 K for 60 h; it was then cooled to 353K at 0.1 K·min^{-1} and then held at 353 K for 40 h. Finally, the container was cooled to room temperature at 0.1 K·min^{-1}. The block-shaped blue crystals were collected by filtration, washed with distilled water (10 mL), and dried under vacuum with a yield of 75%. Anal. for $C_2H_6CuO_6$. Calcd. (%): C 12.67, H 3.19; Found (%): C 12.73, H 3.01. FTIR (KBr pellet): υ_{O-H}, 3436 (br, s); $\upsilon_{C=O}$, 1709(s); υ_{COO^-}, 1584(vs, as), 1386(s, sy); δ_{COO^-}, 791(m).

1.2 Instruments and conditions

Elemental analysis was conducted on a Flash EA 1112 full-automatic microanalyzer. The FTIR spectra were recorded on a Bruker Equinox 55 infrared spectrometer using KBr pellet in the range of 4000−400 cm^{-1}, with a resolution of 4 cm^{-1}. DSC analyses were performed using a CDR-4P Differential Scanning Calorimeter (Shanghai Tianping Instrument Factory, China) and a Pyris 1 Differential Scanning Calorimeter (Perkin Elmer, USA). The conditions were as follows: for CDR-4P, under static air condition and heating rates of 2, 5, 10, and 15 K·min^{-1}; for Pyris 1 DSC, high pure nitrogen was used as purge gas with a flow rate of 20 mL·min^{-1} and a heating rate of 10 K·min^{-1}. The TG and DTG analyses were conducted using a Pyris 1 Thermogravimetric Analyser (Perkin Elmer, USA) using highly pure nitrogen as the purge gas with a flow rate of 20 mL·min^{-1} and a heating rate of 10 K·min^{-1}. In the case of Pyris 1 DSC, the crystal sample was powdered and sealed in an aluminum pan, but in the case of Pyris 1 TGA, the crystal sample was powdered and placed in a platinum sample pan.

1.3 Crystal structure determination

A block-shaped blue single crystal with dimensions of 0.24 mm×0.20 mm×0.16 mm was mounted on the Bruker SMART-10000 CCD area detector diffractometer with graphite monochromated Mo K_α radiation (λ=0.071073 nm) and φ/ω scanning mode at 294(2) K. A total of 1594 reflections were used to determine the cell parameters and the orientation matrix. The crystal was in monoclinic system, $P2_1/c$ space group with crystal parameters of a=0.8533(2) nm, b=0.7151(2) nm, c=0.9463(2) nm, and β=96.94(0)°. The empirical formula is $C_2H_6CuO_6$, M_r=189.61, V=0.5732(2) nm^3, Z=4, D_c=2.197 g·cm^{-3}, μ(Mo K_α)=3.769 mm^{-1}, and F(000)=380. The intensity data were collected in the range of 2.40°≤θ≤26.38° with limiting indices −10≤h≤8, −8≤k≤7, −11≤l≤10. There were 1166 unique reflections [R_{int}=0.0373] and 951 reflections [$I>2\sigma(I)$] in the 3111 collected reflections. Lp and semiempirical corrections were carried out on all data. The data/restraints/parameters were 1166/0/102, S (goodness-of-fit on F^2)=0.996; the R indices for all data were R_1=0.0341, and wR_2=0.0750; the final R indices [$I>2\sigma(I)$] were R_1=0.0273, and wR_2=0.0697. The largest difference peak and hole were 843 and −759 e·nm^{-3}. The structure was solved by direct methods using the SHELXS 97 program[18] and was refined by the full-matrix least squares on F^2 using the SHELXL 97 program[19]. All nonhydrogen atoms were obtained from the difference Fourier map and were refined anisotropically. The hydrogen atoms were obtained from the difference Fourier map or positioned geometrically and treated as riding on the parent atoms or were constrained in the locations during refinements.

2 Results and discussion

2.1 Thermal analyses

2.1.1 Thermal decomposition of polymer 1

There was one endothermic peak and one exothermic peak in each of the four DSC curves of polymer **1** under static air condition at heating rates of 2, 5, 10, and 15 K·min^{-1} (Fig.1). The onset temperatures and the peak temperatures are listed in Table 1. On the basis of these values, the endothermic process is predicted as the dehydration of two coordinated water molecules with E_a of 105.55 kJ·mol^{-1} and the exothermic process is predicted as the decomposition of the coordination polymer with E_a of 101.10 kJ·mol^{-1}. The details of the two processes are shown in the following TG-DTG analyses. The kinetic parameters for the two processes calculated using Kissinger's method[20] and Ozawa's method[21] are listed in Table 1.

In the TG-DTG curves of polymer **1** (Fig.2), there are two main mass loss stages. The first mass loss with 18.73% starts at 358.48 K and ends at 424.02 K, while reaching its highest

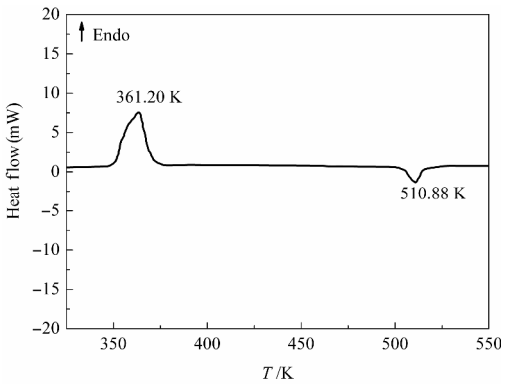

Fig.1 DSC curve of polymer **1** in static air at a heating rate of 10 K·min^{-1}