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Thermal decomposition and dehydration kinetic studies on hydrated Co(II) methanesulfonate

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Abstract

The synthesis, characterization and thermal decomposition studies of Co(II) methanesulfonate are reported. The prepared salt was characterized by Fourier transform infrared (FTIR). The thermal decomposition process was studied using thermogravimetry (TG) and differential scanning calorimetry (DSC) techniques. It can be verified that Co(II) methanesulfonate contains four molecules of crystallization water, which eliminates in two steps. Under heating Co(II) methanesulfonate suffers three main processes: dehydration, thermal degradation and oxide formation. During thermal degradation, the anhydrous salt decomposes to the mixture of $CoSO_4$, Co_3O_4 and CoO in the range of 365–480 °C. At about 800 °C, the decomposed residue was identified as Co_3O_4 by X-ray powder diffraction (XRD). The dehydration kinetics of hydrated Co(II) methanesulfonate was studied by TG technology. The activation energies E_α of two stages dehydration were estimated by isoconversional methods of Friedman, Ozawa and KAS.

Keywords: Thermal decomposition; TG; DSC; XRD; Kinetics

1. Introduction

Metallic sulfonates are recently gaining more and more interest because of its wide utility. For example, coordination compounds of lanthanide methanesulfonates and picoline-*N*-oxides have spectroscopic property (luminescence) [1]. Ceric methanesulfonate has been used in forming quinines and aromatic aldehydes of ketones by an improved electrochemical oxidation process [2]. The first work dealing with the methanesulfonate anion ($CH_3SO_3{}^-$) was developed by Dawson et al. Caesium and sodium methanesulfonates have been previously investigated from a spectroscopic point of view [3]. Aricó et al. have investigated the methanesulfonates of La(III), Nd(III), Er(III), Yb(III), providing very important information about the structures, chemical and physical properties of such class of compounds [4]. However, there are a few works on the thermal behavior of metallic sulfonates. Ramírez et al. have investigated the thermal decomposition of Co(II), Cu(II) and Zn(II) tetrahydrated methanesulfonates [5,6]. Furthermore, Gd(III) and Lu(III) methanesulfonates have been studied, from both, thermal decomposition and dehydration kinetics [3].

Dehydration of solids is the subject of many kinetic studies. It helps to understand the following decomposition mechanism: $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$. Therefore, there are many papers devoted to dehydration of inorganic salts as well as organic substances and metal complexes of organic ligands [7]. In many methods of kinetic estimation, isoconversional method is recommended as a trustworthy way of obtaining reliable and consistent kinetic information [8]. It is a 'model-free' method, which involves measuring the temperatures corresponding to fixed values of α from experiments at different heating rates, β. Recently, we have initiated a study of thermal decomposition and dehydration kinetics of hydrated Co(II) methanesulfonate by thermal analysis technology. The activation energies E_α are calculated according to the isoconversional methods of Friedman [9], Ozawa [10] and Kissnger–Akahira–Sunose (KAS) [11].

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2. Experimental

2.1. Preparation of complexes

All reagents were of analytical grade and were employed without further purification.

The Co(II) methanesulfonate was synthesized by the reaction between methanesulfonic acid and slightly excess basic cobaltous carbonate. CH_3SO_3H–H_2O (v/v = 1:3) was added into flask on magnetic stirrer, and basic cobaltous carbonate was added slowly until no bubble was evolved. The solution was refluxed with stirring for 1 h. The solution obtained was concentrated, filtered and allowed to crystallize in air at room temperature. The products were purified by successive recrystallizations.

Cobalt (II) sulfate was purchased from Sinopharm Chemical Reagent Co. Ltd.

The methanesulfonic group $CH_3SO_3^-$ is represented as MS in this paper.

2.2. Instrument

FTIR spectrum was obtained in KBr discs on a Perkin-Elmer Spectrum GX. Sixteen scans were co-added with a resolution of 4 cm^{-1}, in the range of 4000–400 cm^{-1}.

TG experiments were recorded on a Perkin-Elmer Pyris 1 TGA. For TG analysis of hydrated $Co(MS)_2$, about 2.5 mg samples were employed. The atmosphere was nitrogen of high purity or dry air, with a flow rate of 20 mL min^{-1}. The selected heating rates were 5, 10, 15 and 20 K min^{-1}. For TG analysis of $CoSO_4 \cdot 6H_2O$, 0.5 mg sample was employed under following experimental conditions: heating rate, 20 K min^{-1}; airflow rate, 20 mL min^{-1}.

DSC studies were carried out on a Perkin-Elmer Diamond DSC, with a heating rate of 20 K min^{-1} under N_2 flow. Weight 1.125 mg sample, and then directly place into an unsealed Al pan for DSC analysis. For ΔH measurements, the DSC system was calibrated with indium (m.p. 156.60 °C; $\Delta H_{fus} = 28.45$ J g^{-1}) and zinc (m.p. 419.47 °C; $\Delta H_{fus} = 108.37$ J g^{-1}).

X-ray power diffraction patterns were obtained with a D/max-RB diffractometer in the 2θ range using graphite-monochromated Cu Kα radiation (40 kV, 100 mA). The step scan mode was performed with a step width of 0.02°, at a rate of 4°/min (2θ).

3. Results and discussion

3.1. FTIR spectrum of $Co(MS)_2 \cdot 4H_2O$

The main infrared bands for the synthesized compounds are summarized in Table 1. All bands confirm the salt synthesized is $Co(MS)_2$.

Table 1
Main infrared bands for the synthesized methanesulfonates

Bands (cm^{-1})	$Co(MS)_2 \cdot 4H_2O$
ν_s(OH) (s)	3370
ν_{as}(CH) (w)	3025
ν_s(CH) (w)	2940
δ_s(HOH) (s)	1650
$\delta_{as}(CH_3)$ (w)	1412
$\delta_s(CH_3)$ (w)	1341
ν_{as}(SO) (s)	1186
ν_s(SO) (m)	1061
$\varpi(CH_3)$ (w)	967
ν(CS) (m)	781

(s) strong; (m) medium; (w) weak; s: symmetric; as: asymmetric.

3.2. Dehydration of $Co(MS)_2 \cdot 4H_2O$

Fig. 1 shows TG, DTG and DSC curves of hydrated $Co(MS)_2$ in nitrogen atmosphere at a heating rate of 20 K min^{-1}. From TG and DTG curves, it can be calculated that hydrated $Co(MS)_2$ contains four crystallization water molecules. Dehydration occurs in two stages with the temperature intervals of 76–96 and 135–180 °C. In the first stage, there is an elimination of 2.0 water molecules followed by the removal of the other remaining 2.0 with respective mass losses of 11.2 and 11.1% (calculated mass loss = 11.2%). Subsequently, the hydration yields to anhydrous $Co(MS)_2$ after about 180 °C.

In DSC curve two distinct endothermic peaks can be observed, which correspond to the two peaks in DTG curve, respectively. As observed the first endothermic peak in DSC curve starts at 76 °C and finishes at 96 °C. Simultaneously, TG and DTG curves show that mass loss of hydrated salt occurs from 76 to 96 °C. Also it is remarkable that the peak temperature of DTG and DSC are almost identical. Generally, hydrated salt dehydrates in two different ways at lower temperature (<100 °C). One is that gas–water evolves directly from the salts, the other is liquid–water emits followed by the gasification of them. So the first single endothermic peak

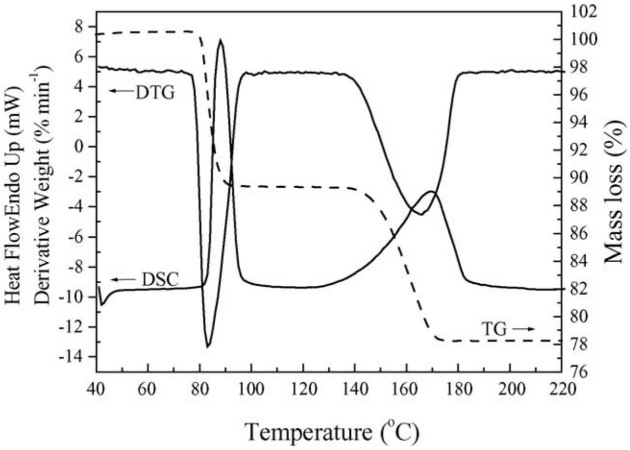

Fig. 1. TG/DTG/DSC curves for dehydration of $Co(MS)_2 \cdot 4H_2O$ in nitrogen atmosphere.

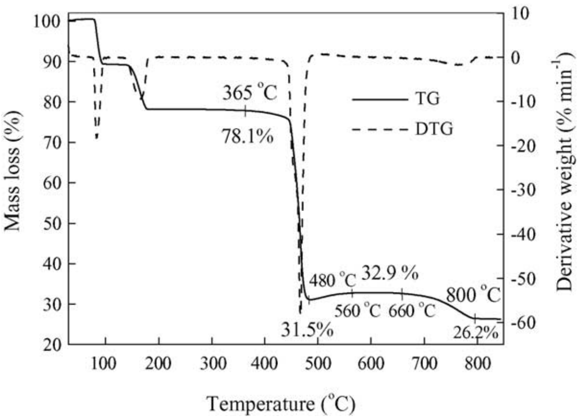

Fig. 2. TG/DTG curves for decomposition of $Co(MS)_2{\cdot}4H_2O$ in air atmosphere.

is the result of the first stage dehydration. In this stage, it is reasonable to conclude that $Co(MS)_2{\cdot}4H_2O$ evolves two gas water directly and the enthalpy corresponded is about 101.1 kJ mol^{-1}. Similarly, the second endothermic peak in DSC curve is due to the loss of the rest crystallization water molecules with the enthalpy of 112.8 kJ mol^{-1}. The whole dehydration processes are as follows:

$$Co(MS)_2{\cdot}4H_2O(s) \rightarrow Co(MS)_2{\cdot}2H_2O(s) + 2H_2O(g) \quad (I)$$

$$Co(MS)_2{\cdot}2H_2O(s) \rightarrow Co(MS)_2(s) + 2H_2O(g) \quad (II)$$

In addition, with the loss of water molecules, the color of the compounds changed from originally pale-pink to pale-violet.

3.3. *Decomposition of $Co(MS)_2$*

The thermal decomposition of $Co(MS)_2{\cdot}4H_2O$ in air atmosphere at 20 K min^{-1} is shown in Fig. 2. It shows that $Co(MS)_2{\cdot}4H_2O$ exhibits five steps decomposition. The first two steps involve dehydration of four water molecules. The last three steps are the decomposition of anhydrous $Co(MS)_2$.

The anhydrous salt, stable up to 365 °C, undergoes an abrupt change in mass loss. The mass fraction of intermediate at 480 °C is 31.5%. It is a mixture of cobalt sulphate, cobalt oxide and cobaltosic oxide, which calculated mass fraction alone were 48.7, 23.3 and 25.0% [5]. Continued heating results in 1.4% increase in weight from 480 to 560 °C. The reason is that CoO progressively translates to Co_3O_4. After stabilizing for a moment, the decomposition of $CoSO_4$ between 660 and 800 °C leads to the formation of Co_3O_4 (mass loss = 6.7%). Therefore, the residue formed at about 800 °C is Co_3O_4 with the content of 26.2% (calculated value = 25.0%). It can be testified by the decomposition of $CoSO_4{\cdot}6H_2O$ in air atmosphere (see Fig. 3). In Fig. 3, $CoSO_4{\cdot}6H_2O$ lose about six water molecules in one step before 270 °C, after stabilizing for a long time, followed by decomposing to black Co_3O_4 in the range of 660–806 °C. In order to further identify the final product, large mounts of hydrated $Co(MS)_2$ was calcined in muffle at 840 °C for 60 min. The product was tested by XRD after cooling. Fig. 4 is the XRD match results of roasted product. As can be seen from Fig. 4, the anhydrous precursors undergo decomposition to form Co_3O_4 indeed. In general, studied $Co(MS)_2{\cdot}4H_2O$ suffers three main processes under heating: dehydration, thermal degradation, and oxide formation. Thus $Co(MS)_2$ decomposes in the following way:

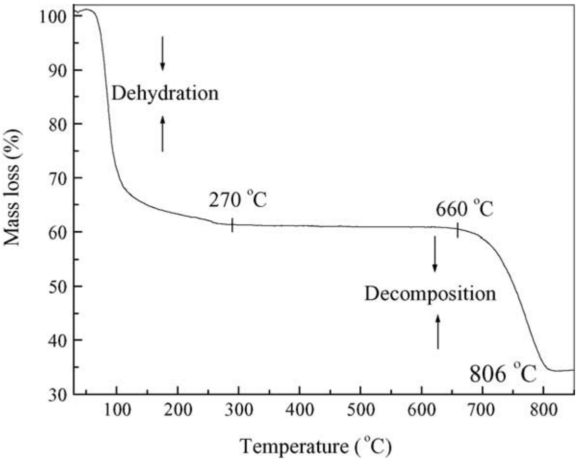

Fig. 3. TG/DTG curves for decomposition of $CoSO_4{\cdot}6H_2O$ in air atmosphere.

$$3Co(MS)_2 \xrightarrow{365\text{–}480\,^{\circ}C} xCoSO_4 + yCoO$$
$$+ zCo_3O_4 \xrightarrow{480\text{–}560\,^{\circ}C} xCoSO_4 + yCo_3O_4 \xrightarrow{660\text{–}800\,^{\circ}C} Co_3O_4$$

3.4. *Activation energy E_α of two steps dehydration*

The kinetic model of dehydration that occurs in non-isothermal conditions is usually described [12] by Eq. (1):

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \qquad (1)$$

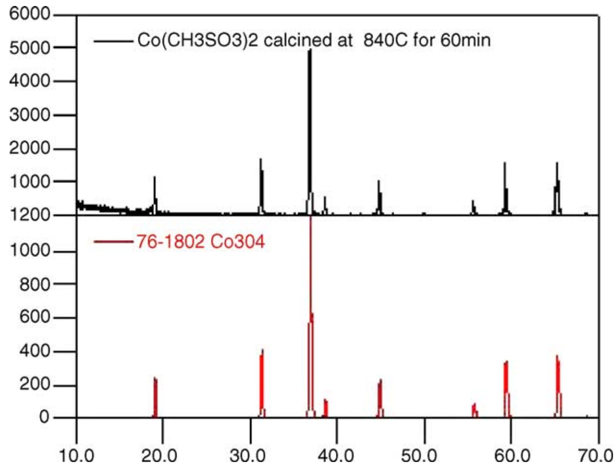

Fig. 4. XRD match results of roasted product at 840 °C for 60min.

Table 2
α–T data at different heating rates, β (K min^{-1})

α	T (K)							
	Step 1				Step 2			
	$\beta = 5$	$\beta = 10$	$\beta = 15$	$\beta = 20$	$\beta = 5$	$\beta = 10$	$\beta = 15$	$\beta = 20$
0.1	344.4	349.0	352.1	354.5	399.9	408.3	414.3	421.4
0.2	344.9	349.5	352.7	355.2	403.6	412.3	418.6	425. 5
0.3	345.2	350.0	353.3	355.9	406.2	415.1	421.6	428.3
0.4	345.6	350.5	353.9	356.4	408.3	417.6	424.2	430.7
0.5	346.0	350.9	354.4	357.0	410.1	419.7	426.5	433.0
0.6	346.4	351.4	355.0	357.8	411.8	421.6	428.4	435.0
0.7	346.8	352.0	355.7	358.5	413.4	423.3	430.4	437.1
0.8	347.4	352.6	356.5	359.7	415.2	425.3	432.4	439.3

where α is the degree of conversion, β the heating rate in K min^{-1}, A the pre-exponential factor in min^{-1}, T the temperature in K, R the gas constant, E the activation energy in kJ mol^{-1}, and $f(\alpha)$ is the reaction model.

In the constant condition of other parameters, the TG curves for dehydration of Co(MS)$_2$·4H$_2$O in N$_2$ at various heating rates ($\beta = 5$, 10, 15 and 20 K min^{-1}) are shown in Fig. 5. According to isoconversional method, the basic data of α and T collected from Fig. 5 are illustrated in Table 2.

The equations used for E_α calculation are:

$$\text{Friedman equation :}\quad \ln\left(\frac{d\alpha}{dt}\right) = \ln[Af(\alpha)] - \frac{E_\alpha}{RT} \qquad (2)$$

$$\text{Ozawa equation :}\quad \log\beta = \log\left[\frac{AE_\alpha}{Rg(\alpha)}\right] - 2.315 - \frac{0.4567E_\alpha}{RT} \qquad (3)$$

$$\text{KAS equation :}\quad \ln\left(\frac{\beta}{T^2}\right) = \ln\left[\frac{AE_\alpha}{Rg(\alpha)}\right] - \left(\frac{E_\alpha}{RT}\right) \qquad (4)$$

where $g(\alpha) = \int_0^\alpha f(\alpha)^{-1}\,d\alpha$ is the integral form of the $f(\alpha)$.

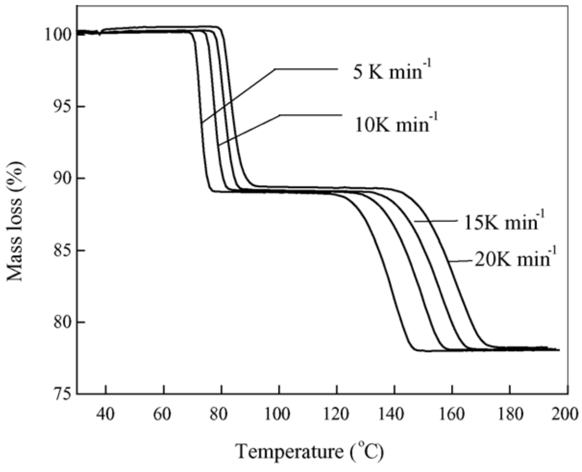

Fig. 5. TG curves for dehydration of Co(MS)$_2$·4H$_2$O at different heating rates in N$_2$.

According to the above mentioned equations, the plots of $\ln(d\alpha/dt)$ versus $1000/T$, $\log\beta$ versus $1000/T$ and $\ln(\beta/T^2)$ versus $1000/T$ corresponding to different conversions α can be obtained by a linear regress of least square method, respectively. The activation energies E_α can be calculated from the slopes of every line with better linear correlation coefficient r. For the two steps dehydration, the slopes change depending on α. The α-dependence of the apparent value of E_α, calculated from the slopes of the Eqs. (2)–(4) at various α, is shown is Table 3. As shown in Table 3, the activation energies calculated by Ozawa method and KAS method are more close to each other and higher than those obtained by Friedman method. Furthermore, the E_α values obtained are almost accordant with those of dehydration of other methanesulfonates [3]. For the first stage dehydration, the observed difference in the activation energies determined by integral and differential methods is bigger. It is because that some systematic errors are obviously introduced in estimation E_α when the latter varies with α [13]. However, in the second stage dehydration,

Table 3
E_a and r calculated by Friedman, Ozawa and KAS methods

α	Friedman method		Ozawa method		KAS method	
	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})	r	E_a (kJ mol^{-1})	r
Step 1						
0.1	101.1	0.994	132.2	0.999	133.2	0.999
0.2	87.3	0.995	130.6	0.999	131.5	0.999
0.3	83.2	0.989	127.1	0.999	127.9	0.999
0.4	80.4	0.988	125.3	0.999	126.0	0.999
0.5	78.8	0.985	123.1	0.999	123.7	0.999
0.6	73.1	0.981	119.6	0.998	119.9	0.998
0.7	72.9	0.982	116.3	0.998	116.5	0.998
0.8	65.1	0.968	111.8	0.997	111.7	0.997
Step 2						
0.1	85.5	0.976	86.8	0.990	84.4	0.989
0.2	83.4	0.997	87.0	0.992	84.6	0.991
0.3	92.2	0.994	87.1	0.994	84.7	0.993
0.4	77.3	0.999	86.7	0.995	84.2	0.995
0.5	78.5	0.998	86.0	0.996	83.4	0.995
0.6	72.3	0.998	86.7	0.996	82.9	0.995
0.7	72.2	0.996	85.5	0.996	81.6	0.995
0.8	68.5	0.995	83.6	0.996	80.8	0.995

the E_α values are almost identify for different α. For this reason, the difference in E_α for integral and differential methods is smaller. Additionally, for the two stages dehydration, the activation energy values vary with the temperature, and higher temperatures are associated with lower activation energies. Such differences could be attributed to the increase in the intra and intermolecular vibrations with the increase in temperature [3,14]. That is, the second dehydration is requiring lower activation energies compared with the first one.

4. Conclusions

$Co(MS)_2 \cdot 4H_2O$ evolves two gas–water directly below 100 °C and the enthalpy corresponded is about 101.1 kJ mol^{-1}. The loss of the rest crystallization water occurs before 180 °C with the enthalpy of 112.8 kJ mol^{-1}. The anhydrous $Co(MS)_2$ decomposes to the mixture of $CoSO_4$, CoO and Co_3O_4 between 365 and 480 °C. At last the residue is Co_3O_4 at about 800 °C.

For the two stages dehydration of $Co(MS)_2 \cdot 4H_2O$, the activation energies calculated by Ozawa method and KAS method are more close to each other and higher than those obtained by Friedman method. For the first stage dehydration, the observed difference in activation energies determined by integral and differential methods is bigger. And the E_α values obtained were almost accordant with those for dehydration of other methanesulfonates. In the second stage dehydration, the difference in E_α for integral and differential methods is smaller. The second stage dehydration is requiring lower activation energies compared with the first one.

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