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RESEARCH OF THERMAL DECOMPOSITION OF HYDRATED METHANESULFONATES

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Abstract

Hydrated methanesulfonates $Ln(CH_3SO_3)_3 \cdot nH_2O$ (*Ln*=La, Ce, Pr, Nd and Yb) and $Zn(CH_3SO_3)_2 \cdot nH_2O$ were synthesized. The effect of atmosphere on thermal decomposition products of these methanesulfonates was investigated. Thermal decomposition products in air atmosphere of these compounds were characterized by infrared spectrometry, the content of metallic ion in thermal decomposition products were determined by complexometric titration. The results show that the thermal decomposition atmosphere has evident effect on decomposition products of hydrated La(III), Pr(III) and Nd(III) methanesulfonates, and no effect on that of hydrated Ce(III), Yb(III) and Zn(II) methanesulfonates.

Keywords: infrared spectra, methanesulfonate, rare earths, thermal decomposition

Introduction

The trifluoromethanesulfonate is a kind of Lewis acid catalyst with good waterfast ability, to which are paid attention in recent years. It is stable and active under common conditions (acidic conditions and room temperature) in organic synthesis. The main advantages of this kind of catalyst in organic synthesis are to improve reactivity and selectivity, simplify separation and recycle the catalysts. It is used for acrylation [1], alkylation [2], nitration [3] and oxidation [4], and good effects have been obtained. However, because of expensive price of triflate acid, its application is limited. In our lab, methanesulfonic acid is used to replace triflate acid to synthesize some methanesulfonates which are used for esterification and alkylation. Here six kinds of hydrated methanesulfonates were synthesized. They can be represented by general formula: $Ln(CH_3SO_3)_3 \cdot nH_2O$; *Ln*=La, Ce, Pr, Nd, Yb and $Zn(CH_3SO_3)_2 \cdot nH_2O$; *n* – number of crystal water. Number of crystal water was determined by thermogravimetry, thermal decomposition products of these compounds in nitrogen and air atmosphere were also investigated. The thermal decomposition products in air atmosphere were characterized by infrared spectrometry, the content of metallic ion in

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these thermal decomposition products was determined by complexometric titration. The effect of atmosphere on the thermal decomposition products was investigated.

Experimental

Materials and sample preparation

All reagents and oxides in this experiment are chemically pure.

Preparation of hydrated La(III), Pr(III), Nd(III), Yb(III) and Zn(II) methanesulfonates: metal oxides and methanesulfonic acid were, respectively, weighed in 1:6 mole ratio (ZnO and methanesulfonic acid in 1:2). Then $CH_3SO_3H–H_2O$(*V/V*=1:1) were added into reactor, oxides were added slowly with stirring for 1 h under the condition of heating and reflux. After evaporation of the water, the solid was dried in vacuum for 3 h at 100°C.

Preparation of hydrated Ce(III) methanesulfonate: CeO_2 and CH_3SO_3H/H_2O (*V/V*=1:1) were added into reactor, the mole ratio of CeO_2 and methanesulfonic acid was 1:3. The mixture was stirred and refluxed for 4~5 h, hydrogen peroxide was added slowly at the same time. After evaporation of the water, the solid was dried in vacuum for 3 h at 100°C.

Methods

TG curves of methanesulfonates were obtained from 40 to 850°C (hydrated Yb methanesulfonate from 40 to 500°C) at the rate of 20°C min^{-1} in nitrogen and air atmosphere on Pyris 1 TGA (Perkin Elmer). According to data of TG curves, methanesulfonates were torrefied for 1 h at 800°C (hydrated Yb methanesulfonate at 500°C) in muffle in air atmosphere. Infrared spectra of the thermal decomposition products were measured in KBr pellets in the region of 2000~400 cm^{-1} using Spectrum GX FT-IR System (Perkin Elmer). Then, the content of metallic ion in these thermal decomposition products were determined complexometrically using EDTA as an agent.

Results and discussion

Calculation for number of crystal water

Value of *n* can be calculated according to the following formula:

$$\text{content of crystal water\%}=100\frac{M_1}{M_2}$$

where M_1 – molecular mass of crystal water; M_2 – molecular mass of hydrated methanesulfonates.

In this experiment, we think the mass loss in the 40~300°C temperature range in TG curves were due to the loss of crystal water, and so content of crystal water% should equal to the mass loss. Then value of *n* can be determined.

Characterization of the thermal decomposition products of hydrated methanesulfonates

Thermogravimetry

Thermogravimetric data of hydrated methanesulfonates are showed in Table 1. It is known from Table 1 that the final mass fraction are not all same in different atmosphere. If we think oxides were obtained, calculated values of thermal decomposition products in nitrogen and air atmosphere of hydrated Ce and Zn methanesulfonates approximate to their respective measured values, their products are respectively CeO_2 [5] and ZnO. In nitrogen atmosphere, the thermal decomposition products of hydrated Pr methanesulfonate are mixtures of Pr_2O_3 and PrO_2 [6], its measured value is just between two its two calculated values; the thermal decomposition products of hydrated La and Nd methanesulfonates are, respectively, La_2O_3 and Nd_2O_3, their calculated values also approximate to their respective measured values. However, in air atmosphere, if we also think so, calculated values of thermal decomposition products of hydrated La, Pr and Nd methanesulfonates are largely different from their respective measured values. Figure 1 clearly shows that the thermal decompositon of $La(CH_3SO_3)_3{\cdot}nH_2O$ is very different at 800 degree celsius under the nitrogen and the air. The reason may be that the thermal decomposition products vary in different atmosphere. Besides measured values thermal decomposition products in nitrogen and air atmosphere of hydrated Yb methanesulfonate are same. And so its products in nitrogen and air atmosphere are also same, but not Yb_2O_3 or $Yb_2(SO_4)_3$ according to its measured values. If we want to know whether different atmosphere influence the thermal decomposition products and what on earth the thermal decomposition products in nitrogen and air atmosphere of hydrated Yb methanesulfonate are, infrared spectrometry can be used to investigate the thermal decomposition products of hydrated methanesulfonates in air atmosphere.

Infrared spectrometry

It was reported [7] that thermal decomposition products of hydrated La(III), Nd(III) and Er(III) methanesulfonates in air atmosphere were, respectively, $(LaO)_2SO_4$,

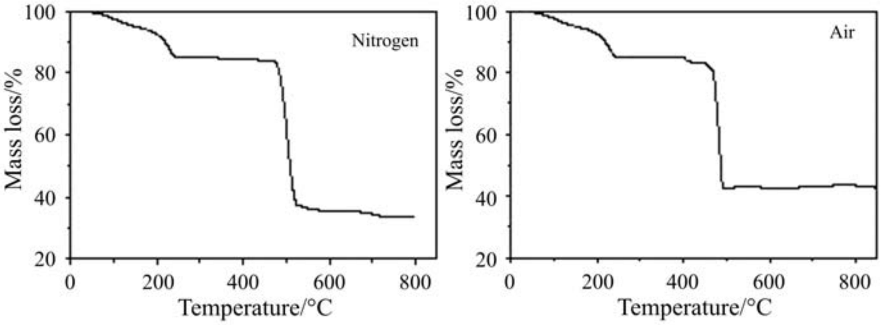

Fig. 1 TG curves of $La(CH_3SO_3)_3{\cdot}nH_2O$ in nitrogen and air atmosphere

Table 1 Thermogravimetric data of hydrated methanesulfonates in nitrogen and air atmosphere

Gas	Hydrated methanesulfonates	Mass loss of crystal water/%	Number of crystal water	Residual mass fraction at 800°C		Thermal decomposition products
				Measured values/%	Calculated values/%	
Nitrogen	$La(CH_3SO_3)_3{\cdot}nH_2O$	14.9837	4	33.65	32.83	La_2O_3
	$Ce(CH_3SO_3)_3{\cdot}nH_2O$	28.1732	9	29.30	28.82	CeO_2
	$Pr(CH_3SO_3)_3{\cdot}nH_2O$	9.0295	2	36.90	35.67; 37.41	Pr_2O_3; PrO_2
	$Nd(CH_3SO_3)_3{\cdot}nH_2O$	7.8817	2	37.63	36.14	Nd_2O_3
	$Yb(CH_3SO_3)_3{\cdot}nH_2O$	10.2249	3	47.71*	46.27	$(YbO)_2SO_4$
	$Zn(CH_3SO_3)_2{\cdot}nH_2O$	18.3315	3	26.64	26.32	ZnO
Air	$La(CH_3SO_3)_3{\cdot}nH_2O$	14.9106	4	42.24	42.44	$(LaO)_2SO_4$
	$Ce(CH_3SO_3)_3{\cdot}nH_2O$	28.6386	9	29.96	28.82	CeO_2
	$Pr(CH_3SO_3)_3{\cdot}nH_2O$	8.1862	2	44.09	44.34	$(PrO)_2SO_4$
	$Nd(CH_3SO_3)_3{\cdot}nH_2O$	6.0190	2	45.37	44.74	$(NdO)_2SO_4$
	$Yb(CH_3SO_3)_3{\cdot}nH_2O$	10.6923	3	47.26*	46.27	$(YbO)_2SO_4$
	$Zn(CH_3SO_3)_2{\cdot}nH_2O$	18.6416	3	26.96	26.32	ZnO

* Residual mass fraction at 500°C

$(NdO)_2SO_4$ and $(ErO)_2SO_4$, their calculated values approximated to their respective measured values. But definite experimental supports have been still lacking. In order to investigate whether above products can be obtained in air atmosphere, hydrated methanesulfonates were torrefied in muffle at 800°C (hydrated Yb methanesulfonate at 500°C) for 1 h in air atmosphere, infrared spectra of their thermal decomposition products are shown in Fig. 2.

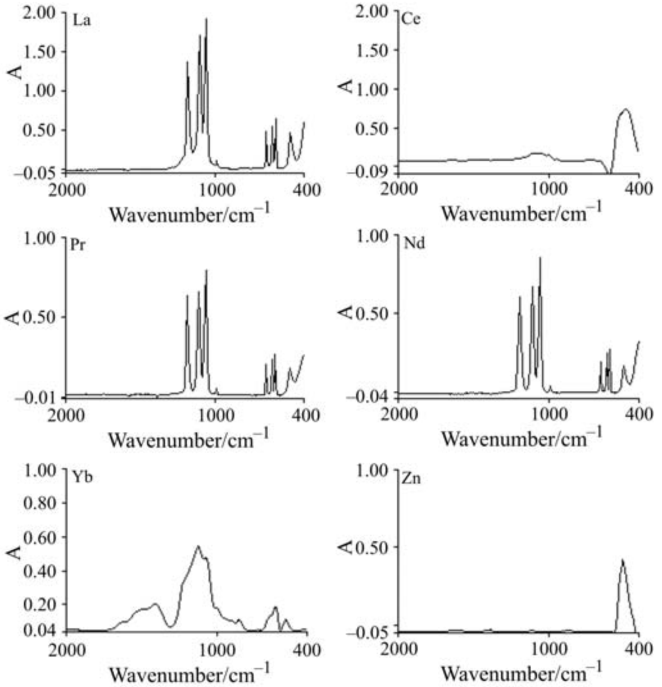

Fig. 2 Infrared spectra of thermal decomposition products of {$Ln(CH_3SO_3)_3 \cdot nH_2O$; *Ln*=La, Ce, Pr, Nd and Yb} and $Zn(CH_3SO_3)_2 \cdot nH_2O$ at 800°C {$Yb(CH_3SO_3)_3 \cdot nH_2O$ at 500°C} in muffle in air atmosphere

It can be seen from Fig. 2 that besides the infrared spectra of the thermal decomposition product of hydrated Ce and Zn methanesulfonates, stretching vibration v(O=S=O) (at 1190 and 1110 cm^{-1}) and stretching vibration v(O–S–O) (at 1065 and 995 cm^{-1}) are found in thermal decomposition products of hydrated La, Pr, Nd and Yb methanesulfonates. This means that the thermal decomposition products of the four RE methanesulfonates in air atmosphere are not simple oxides but compounds containing sulfate radial group. In view of reference [7], it can be though that thermal decomposition products of hydrated La, Pr, Nd and Yb methanesulfonates in air atmosphere are respectively $(LaO)_2SO_4$, $(PrO)_2SO_4$, $(NdO)_2SO_4$ and $(YbO)_2SO_4$. In this way, calculated values of hydrated La, Pr and Nd methanesulfonates approximate to their respective measured values. This also means that above products can be surely obtained in air atmosphere. Because the thermal decomposition products in nitrogen and air atmosphere of hydrated Yb methanesulfonates are same, its thermal decomposition product in nitrogen atmosphere is also $(YbO)_2SO_4$.

Complexometric titration for the content of metallic ion in thermal decomposition products in air atmosphere

Here, only thermal decomposition product in air atmosphere of hydrated La methanesulfonate is taken as an example for explanation. The content of La in the thermal decomposition product in air atmosphere of hydrated La methanesulfonate was determined by complexometric titration using standard EDTA solution. The result is 68.94% which approximate to the content of La in $(LaO)_2SO_4$, 68.45%. This also means that the thermal decomposition product of hydrated La methanesulfonate in air atmosphere is surely $(LaO)_2SO_4$. The content of metallic ion in thermal decomposition products of the other five methanesulfonates in air atmosphere can also be determined in the same way.

Discussion on decomposition process

Egashira *et al.* [8] have studied thermal decomposition in static air of $\{Ln(CF_3SO_3)_3\cdot 9H_2O;\ Ln=La\text{–}Lu\}$ systematically. They thought that thermal decomposition process in static air $Ln(CF_3SO_3)_3$ can be shown as follows:

$$Ln(CF_3SO_3)_3 \rightarrow LnF_3+3SO_2+CO_2+CF_3OCF_3$$

The final residual products are LnF_3. However, it can be seen obviously from this experiment that the thermal decomposition products in air atmosphere of $\{Ln(CH_3SO_3)_3\cdot nH_2O;\ Ln=La, Ce, Pr, Nd \text{ and } Yb\}$ and $Zn(CH_3SO_3)_2\cdot nH_2O$ are quite different from that of $Ln(CF_3SO_3)_3$. Possible decomposition processes in air atmosphere of $Ln(CH_3SO_3)_3$ and $Zn(CH_3SO_3)_2$ can be shown as follows:

$$2Ln(CH_3SO_3)_3+3O_2 \rightarrow (LnO)_2SO_4+5SO_2+6CO_2+6H_2O \quad Ln=La, Pr, Nd \text{ and } Yb;$$

$$4Ce(CH_3SO_3)_3+19O_2 \rightarrow 4CeO_2+12SO_2+12CO_2+18H_2O$$

$$Zn(CH_3SO_3)_2+3O_2 \rightarrow ZnO+2SO_2+2CO_2+3H_2O$$

Conclusions

Thermal decomposition products of hydrated La(III), Ce(III), Pr(III), Nd(III), Yb(III) and Zn(II) methanesulfonates in nitrogen and air atmosphere are studied in this paper. According to the results of thermogravimetry, infrared spectrometry and complexometric titration, thermal decomposition products of hydrated La(III), Pr(III) and Nd(III) methanesulfonates vary in nitrogen and air atmosphere: in nitrogen atmosphere, thermal decomposition products of hydrated Pr(III) methanesulfonate is mixtures of Pr_2O_3 and PrO_2, that of hydrated La(III) and Nd(III) methanesulfonates are, respectively, La_2O_3 and Nd_2O_3; in air atmosphere, thermal decomposition products of hydrated La(III), Pr(III) and Nd(III) methanesulfonates in air atmosphere are, respectively, $(LaO)_2SO_4$, $(PrO)_2SO_4$ and $(NdO)_2SO_4$. The thermal decomposition products of hydrated Ce(III) methanesulfonate in nitrogen and air atmosphere are all CeO_2. The thermal decomposition products in nitrogen and air atmosphere of hydrated Yb(III) methanesulfonate are all $(YbO)_2SO_4$. The thermal decomposition products in nitrogen and air atmosphere of hydrated Zn(II) methanesulfonate are all ZnO.

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