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CHARACTERISTICS OF THERMAL DECOMPOSITION PRODUCTS OF RARE EARTH, ALKALI EARTH METAL AND TRANSITION METAL *p*-TOLUENESULFONATES

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A series of alkali earth (Ca, Ba), lanthanide (La, Ce, Pr, Nd,) and transition metal (Fe, Mn, Co, Ni, Cu, Zn, Cd) *p*-toluenesulfonates were synthesized. Thermal analysis, infrared spectrophotometry, and XRD powder diffraction patterns were employed to characterize the final thermal decomposition products. By heating in dynamic air atmosphere at 30–850°C, it has been found that the alkali earth *p*-toluenesulfonates thermal decompose ending with sulphates $CaSO_4$ and $BaSO_4$, while the lanthanide *p*-toluenesulfonates with oxosulphates $(LaO)_2SO_4$, $(PrO)_2SO_4$, $(NdO)_2SO_4$ and CeO_2. Only the transition metal *p*-toluenesulfonates, decompose ending with appropriate metal oxides in all cases.

Keywords: *alkali earth, lanthanide, p-toluenesulfonates, thermal decomposition products, transition metal*

Introduction

It is well known that the area of metal sulfonates has been developed rapidly and has become a fascinating subject of interest. This stems from a broad range of promising applications, such as in the areas of ion exchange [1], electrochemistry [2], and catalysis [3, 4], etc. So far, the thermal behaviors of some transition metal alkanesulfonate have been studied [5, 6]. Aricó *et al*. have reported the structures of some rare earth methanesulfonates [7]. The structures of divalent transition metal sulfonate complexes with *o*-phenanthroline were investigated [8]. Regarding the copper sulfonates, the stoichiometry and kinetics of thermal decompositions for some of them have been studied [9].

Quite recently, Santos *et al*. systematically studied the dehydration of all the rare earth *p*-toluenesulfonates [10] and the thermal decomposition of the lanthanoid (*Ln*=La–Lu) trifluoromethanesulfonate complexes was studied [11]. Lee *et al*. investigated the mercury *p*-toluenesulfonate used in the direct transformation of aromatic ketones into oxazoles [12]. However, to the best of our knowledge, a detailed investigation has not been made on the final thermal decomposition of the title materials. The orientation of this paper is to study the thermal decomposition of them under dynamic air atmosphere in detail.

Experimental

Sample preparation

p-Toluenesulfonic acid (analytical grade, >99%) were completely dissolved in deionized water and heated to 50°C. Under stirring, the excess carboxylates (Ca, Ba, Mn, Cd), hydroxycarbonate or oxides (Co, Ni, Cu, Zn, La, Pr, Nd) was added respectively, then heated to 80–90°C. After heated at 80–90°C for about 3 h. The hot solution was filtered. The product was crystallized from the filtrate after cooling. After recrystallisation with water, the products obtained were dried at room temperature for a week. Ferrous *p*-toluenesulfonate was prepared by reacting excess iron powder with *p*-toluenesulfonic acid solution under refluxing temperature. After filtration and cooling, the product was crystallized from water and the crystal was recrystallized with water, and dried at room temperature for two days.

Methods and apparatuses

The samples of alkali earth (Ca, Ba) and lanthanide (La, Pr, Nd) *p*-toluenesulfonates were calcinated isothermally in 50 mL ceramic crucibles in a muffle furnace at 700°C for 30 min. $CaSO_4 \cdot 2H_2O$ (analytical grade) was also calcinated under above conditions. The decomposition residues of these samples are subjected to XRD and FTIR analysis.

The TG experiments were performed by using a PerkinElmer Pyris 1 thermogravimetric analysis (TG) in a dynamic air atmosphere (20 mL min^{-1}) at temperature range 30–850°C with a heating rate 20 K min^{-1}. Ceramic crucibles for TG were used and the sample powder mass is 2–3 mg.

The FTIR spectra of the decomposition products were recorded on a PerkinElmer spectrophotometer with resolution of 4 cm^{-1} in the wave number range

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Table 1 Thermogravimetric data of *p*-toluenesulfonates in dynamic air atmosphere

p-Toluenesulfonate	*x*	Residue mass fraction /%		Final residues and color characteristic of them	
		found	calc.		
Mn(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	6	15.75	15.62	Mn_2O_3	black
Fe(p-$CH_3C_6H_4SO_3)_2\cdot H_2O$	6	15.55	15.77	Fe_2O_3	red
Co(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	6	15.83	15.76	Co_3O_4	black
Ni(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	6	14.37	14.67	NiO	green
Cu(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	6	15.58	15.48	CuO	black
Zn(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	5	15.93	16.35	ZnO	white
Cd(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	0	27.58	28.24	CdO	white
Ca(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	0.5	34.45	34.76	$CaSO_4$	white
Ba(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	0	47.43	48.64	$BaSO_4$	white
La(p-$CH_3C_6H_4SO_3)_2\cdot xH_2O$	2	30.59	30.68	$(LaO)_2SO_4$	white
Ce(p-$CH_3C_6H_4SO_3)_3\cdot xH_2O$	2	25.16	24.96	CeO_2	yellow
Pr(p-$CH_3C_6H_4SO_3)_3\cdot xH_2O$	2	30.02	29.68	$(PrO)_2SO_4$	white
Nd(p-$CH_3C_6H_4SO_3)_3\cdot xH_2O$	2	30.55	30.02	$(NdO)_2SO_4$	white

2000–400 cm^{-1}. The samples calcined were prepared as KBr diluted pellets in the solid-state.

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

Results and discussion

Thermogravimetry analysis

Table 1 presents a summary of the thermogravimetric analytical results. Typical TG and DTG curves of calcium and lanthanum *p*-toluenesulfonates are shown in Fig 1. Generally, the thermal decomposition products of the oxy salts are corresponding oxides [13]. However, if the final products of thermal decomposition are assumed as CeO_2, Nd_2O_3, Pr_6O_{11} and La_2O_3, there are great differences between the theoretical values and experimental values except CeO_2. So the results obtained from the TG curve indicate that the final decomposition products of lanthanide compounds are not all the corresponding oxides. According to the literature [14], the thermal decomposition products of La, Pr and Nd methanesulfonates possibly are $(LaO)_2SO_4$, $(PrO)_2SO_4$ and $(NdO)_2SO_4$. From the thermogravimetric analytical results (Table 1), it is suggested that the experimental mass fractions of the oxide residues are in accordance with that of calculated values, which supports the proposed final products of oxosulfates.

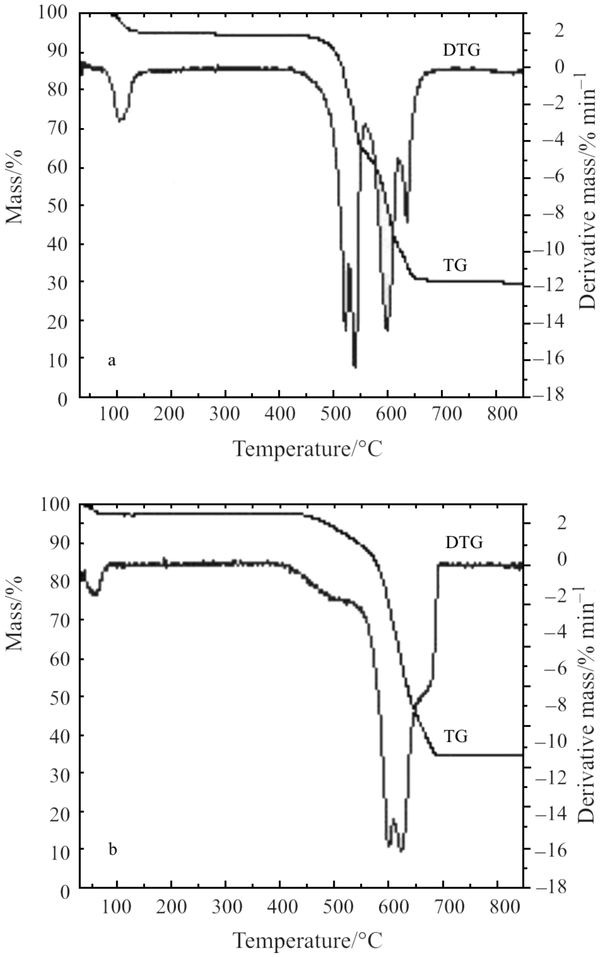

Fig. 1 TG and DTG curves a – calcium *p*-toluenesulfonate and b – lanthanum *p*-toluenesulfonate in dynamic air atmosphere

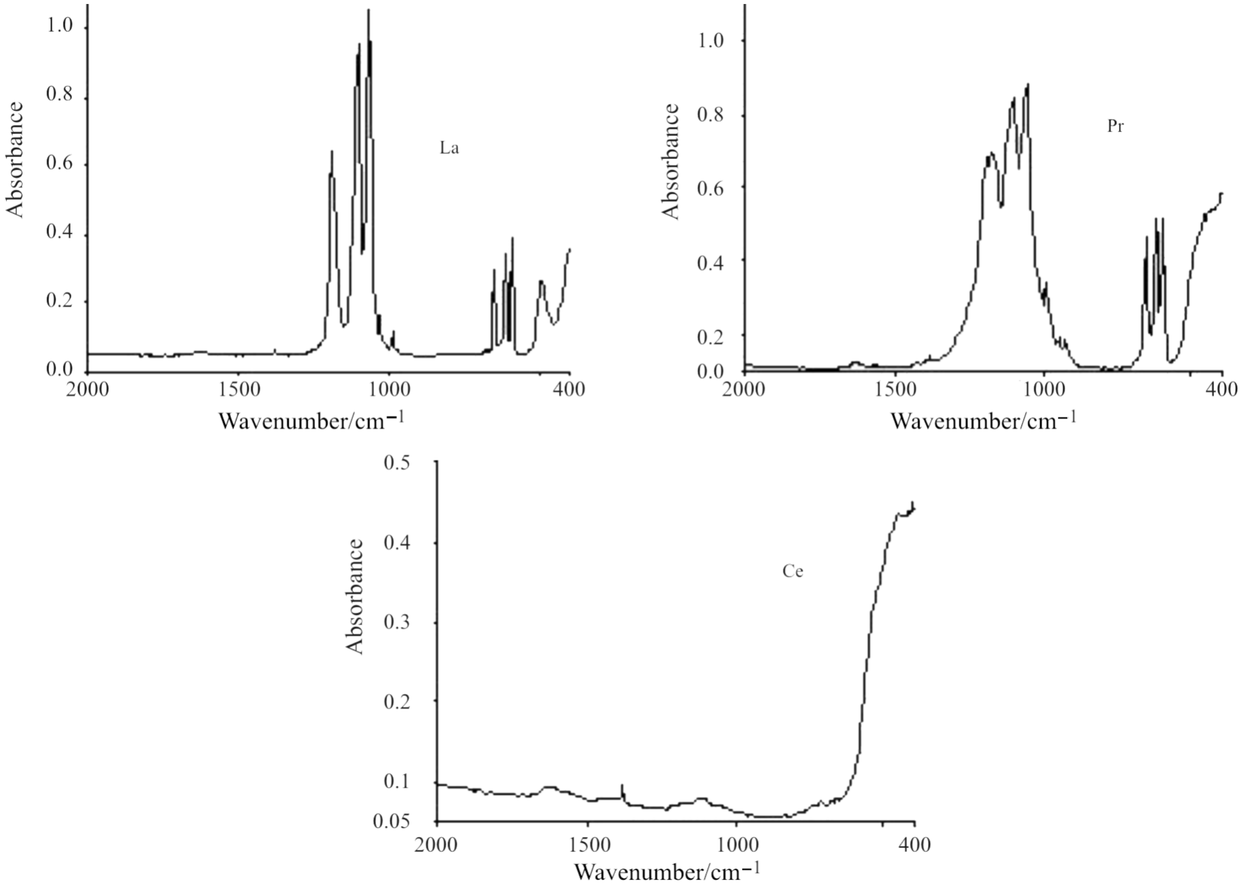

Fig. 2 Infrared spectra of the calcined residue of lanthanum, praseodymium and cerium *p*-toluenesulfonates

For the alkali earth *p*-toluenesulfonates, the final decomposition product of CaO and BaO (calc.: 14.66%, 31.96%; found: 47.43%, 34.45%) is also impossible. As demonstrated in the literature [15], it is possible to conclude that there are intermediate formations of sulphate or oxosulphate during heating the alkali earth *p*-toluenesulfonates. The high thermal stability of the $BaSO_4$ and $CaSO_4$ makes it possible to suppose that the final thermal decomposition residues of alkali earth *p*-toluenesulfonates are sulphate salts. In the thermogravimetric analytical results (Table 1), the experimental content is well agreed with the expected ones.

In the case of transition metal *p*-toluenesulfonates, because of transition metal exhibiting different oxidation states, it is difficult to infer the specific final products of thermal decomposition. The final product of each sample is discussed separately in the following way.

It is well known that oxidation states of cadmium and zinc *p*-toluenesulfonates generally are +2. The final products of them should be ZnO and CdO. For nickel and copper *p*-toluenesulfonates, color characteristic of the final residues can be employed to infer the types of oxides formation. The final product of thermal decomposition of ferrous *p*-toluenesulfonate is red Fe_2O_3 because FeO and Fe_3O_4 are all black, while that of nickel *p*-toluenesulfonate is green NiO (Ni_2O_3 is black) and that of copper *p*-toluenesulfonate is black CuO (Cu_2O is red). As to cobalt and manganese *p*-toluenesulfonates, Co_3O_4 and Mn_2O_3 were found to be the final products of appropriate *p*-toluenesulfonates. In Table 1, the experimental mass fractions of the final products all match with that of the theoretical calculations, and consequently confirm above description.

Infrared spectrometry analysis

From TG curves, the unexpected results were obtained, namely, sulfate salts are the final thermal decomposition products of alkali earth *p*-toluenesulfonates and oxosulphates or oxide are that of lanthanide *p*-toluenesulfonates. To further confirm this conclusion from TG experiments, the parent samples were calcinated isothermally in ceramic crucibles in a muffle furnace at 700°C for 30 min (determined from TG curves shown in Fig. 1). Figure 2 presents typical IR spectra of the residue of calcined lanthanum and praseodymium *p*-toluenesulfonate.

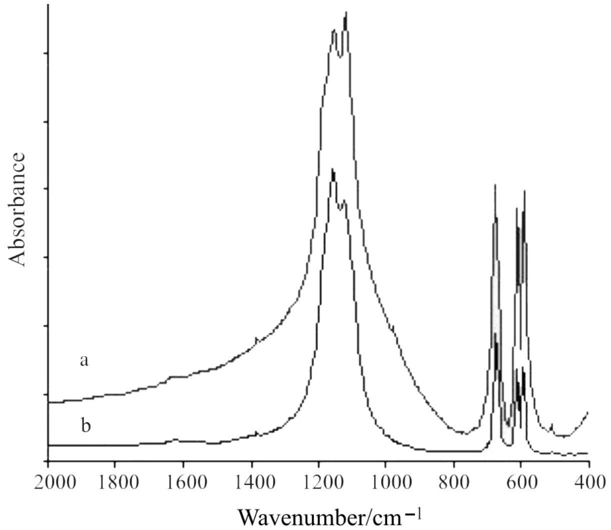

Fig. 3 Infrared spectra of the residue of a – calcium *p*-toluenesulfonate calcined and that of b – analytical grade $CaSO_4 \cdot 2H_2O$

Spectral analyses of the thermal decomposition residues of lanthanum and praseodymium *p*-toluenesulfonates reveal that they do exhibit characteristic absorption bands of sulphate ions. The triplet between 1050 cm^{-1} and 1120 cm^{-1} is assigned to the triply degenerate mode of vibrations of sulfate ions (1191, 1103, 1064 cm^{-1} for La and 1178, 1102, 1059 cm^{-1} for Pr), while the other triply degenerate vibrations of sulphate ions occur between 590 and 660 cm^{-1} (657, 618, 594 cm^{-1} for La and 656, 618, 596 cm^{-1} for Pr) [16]. However, it can be seen from Fig. 2 that there is no characteristic absorption bands of sulphate ions in the residue of cerium *p*-toluenesulfonate. This feature is indicative of the fact that the thermal decomposition products identified by TG curves provides further support from the infrared spectra analysis.

For the calcined residues of alkali earth *p*-toluenesulfonates, take calcium salt for example, a parallel experiment was carried out. $CaSO_4 \cdot 2H_2O$ (analytical grade) was also calcinated under the same calcining condition of the calcium *p*-toluenesulfonate applied, and the IR spectra of the two residues were shown in Fig. 3. It can be obviously seen from Fig. 3 that the two infrared spectra are approximately the same, which supporting the conclusion from TG experiment.

XRD analysis

In order to characterize the thermal decomposition products of the samples investigated more fully, X-ray diffraction techniques were used. The calcined samples obtained as described in IR experiments are subjected to XRD studies. Comparisons of the spectra of the calcined residues with standard spectra based on the identified results of TG and FTIR techniques were shown in Fig. 4.

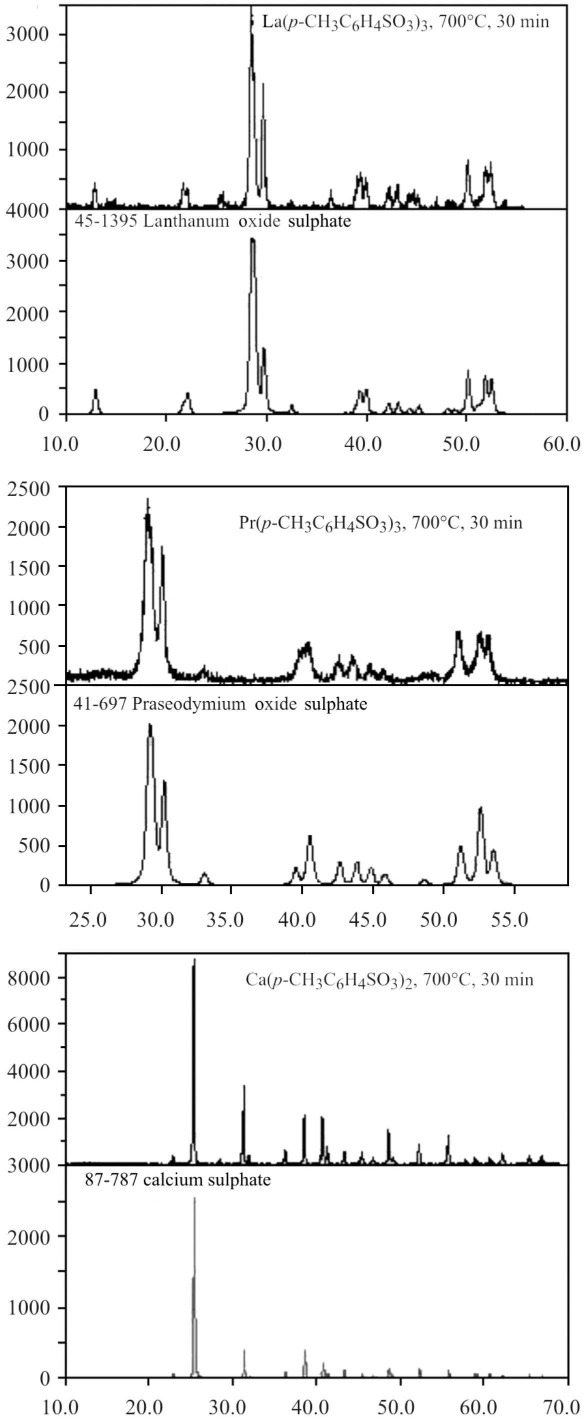

Fig. 4 Comparison of the XRD spectra of thermal decomposition product with the standard spectra

The XRD spectra clearly show the correctness of the final products of thermal decomposition identified by TG and IR analysis. Hence, the final products of thermal decomposition of alkali earth *p*-toluenesulfonates and lanthanide *p*-toluenesulfonates are believed to be corresponding sulphates and oxosulphates respectively rather than simple oxides.

Conclusions

Thermal decomposition products of alkali earth (Ca, Ba), lanthanide (La, Ce, Pr, Nd,) and transition metal (Fe, Mn, Co, Ni, Cu, Zn, Cd) *p*-toluenesulfonates were well explored in this paper. The analysis of thermal decomposition products of the above *p*-toluenesulfonates leads to the following conclusions: there is remarkable difference in the final decomposition products of the three types metal *p*-toluenesulfonates. The type of the thermal decomposition products of the title samples prepared depends on the metal ion in the parent material.

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