J Therm Anal Calorim (2009) 98:801–806
DOI 10.1007/s10973-009-0119-z

Thermal decomposition of metal methanesulfonates in air

M. Wang · Z. G. Song · H. Jiang · H. Gong

Received: 8 May 2009 / Accepted: 21 May 2009 / Published online: 9 July 2009

Abstract The thermal decompositions of dehydrated or anhydrous bivalent transition metal (Mn, Fe, Co, Ni, Cu, Zn, Cd) and alkali rare metal (Mg, Ca, Sr, Ba) methanesulfonates were studied by TG/DTG, IR and XRD techniques in dynamic Air at 250–850 °C. The initial decomposition temperatures were calculated from TG curves for each compound, which show the onsets of mass loss of methanesulfonates were above 400 °C. For transition metal methanesulfonates, the pyrolysis products at 850 °C were metal oxides. For alkali rare metal methanesulfonates, the pyrolysis products at 850 °C of Sr and Ba methanesulfonates were sulphates, while those of Mg and Ca methanesulfonate were mixtures of sulphate and oxide.

Keywords Methanesulfonates · Thermal decomposition · Transition metal · Alkali earth metal

Introduction

Methanesulfonate, a water-tolerant Lewis acid catalyst has drawn much attention due to its excellent advantages such as reactivity, selectivity and reuse in organic synthesis. It showed good effects in the esterification [1], Biginelli reaction [2, 3], diacetoxylation [4] and tetrahydropyranylation [5], etc. So far, the structure and thermal behaviors of them have been studied. For example, Aricó et al. [6, 7] have investigated the structure and properties of hydrated and anhydrous rare earth metal (La, Ce, Nd, Sm, Tb, Er, Yb) methanesulfonates. Charbonnier studied the thermal behavior of transition metal methanesulfonate (Cu, Zn, Mn, Cd, Ag) under an inert atmosphere [8]. Tian et al. [9] have reported the pyrolysis products of rare earth metal (La, Ce, Pr, Nd, Yb) methanesulfontes in N_2 and Air atmosphere. Moura et al. [10] reported the degradation of gadolinium and lutetium methanesulfonates. Recently, We also reported the dehydration studies of Co, Cu and Zn methanesulfonates in N_2 atmosphere [11]. However, to the best of our knowledge, there is no systematic study on the thermal decomposition of the title materials in Air atmosphere. In this paper, we study the thermal stability and thermal decomposition products at 850 °C in dynamic Air atmosphere for representative dehydrated or anhydrous bivalent transition metal (Mn, Fe, Co, Ni, Cu, Zn, Cd) and alkali earth metal (Mg, Ca, Sr, Ba) methanesulfonates using TG/DTG, IR and XRD techniques.

Experimental

Sample preparation

The methanesulfonates were prepared in aqueous solution by the reaction of methanesulfonic acid (analytical grade, >99.0%) and metallic oxide (Cu, Zn, Mg, Ca, Ba), carbonate (Mn, Co, Cd, Sr) or metal substance (Fe, Ni). After heated at 80–90 °C for about 3 h, the hot solution was filtered. The filtrate was concentrated and allowed to

M. Wang (✉)
College of Chemistry and Chemical Engineering,
Bohai University, Jinzhou 121000, People's Republic of China
e-mail: minwangszg@yahoo.com.cn

Z. G. Song
Center for Science & Technology Experiment, Bohai University,
Jinzhou 121000, People's Republic of China

H. Jiang · H. Gong
Liaoning Shihua University, Fushun 113001,
People's Republic of China

crystallize in air at room temperature. The products were purified by successive recrystallization with water. Elemental analysis, complexometric titration, IR, and thermal analysis techniques are used for characterization of the methanesulfonates. Analytical results were listed in Table 1. The stoichiometric formula of the compounds is $M(CH_3SO_3)_2 \cdot xH_2O$. The crystallization water of all $M(CH_3SO_3)_2 \cdot xH_2O$ can be removed and determined by TG in the temperature range 30–250 °C with a heating rate 20 K min^{-1}. Therefore, the anhydrous bivalent $M(CH_3SO_3)_2$ studied in this paper were obtained.

Apparatuses

The TG experiments were performed by using a Perkin Elmer 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 Perkin Elmer spectrophotometer with resolution of 4 cm^{-1} in the wave number range 2000–400 cm^{-1}.

Table 1 Analytical results of $M(CH_3SO_3)_2 \cdot xH_2O$

$M(CH_3SO_3)_2 \cdot xH_2O$	Found mass%			Calcd. mass%		
	M	S	H_2O	M	S	H_2O
$Mn(CH_3SO_3)_2 \cdot 2H_2O$	19.57	22.84	12.48	19.54	22.81	12.82
$Fe(CH_3SO_3)_2 \cdot 4H_2O$	17.49	20.12	23.56	17.56	20.16	22.66
$Co(CH_3SO_3)_2 \cdot 4H_2O$	18.41	19.97	22.08	18.35	19.96	22.44
$Ni(CH_3SO_3)_2 \cdot 4H_2O$	18.32	20.02	21.96	18.29	19.98	22.50
$Cu(CH_3SO_3)_2 \cdot 4H_2O$	19.55	19.63	22.07	19.51	19.68	22.12
$Zn(CH_3SO_3)_2 \cdot 4H_2O$	20.01	19.64	21.90	19.96	19.57	21.99
$Cd(CH_3SO_3)_2 \cdot 2H_2O$	33.25	18.98	10.20	33.20	18.94	10.64
$Mg(CH_3SO_3)_2 \cdot 2H_2O$	9.51	25.45	16.08	9.70	25.59	14.39
$Ca(CH_3SO_3)_2$	17.37	27.88	0	17.41	27.85	0
$Sr(CH_3SO_3)_2 \cdot 3H_2O$	26.34	19.29	17.30	26.40	19.32	16.29
$Ba(CH_3SO_3)_2$	41.96	19.54	0	41.93	19.58	0

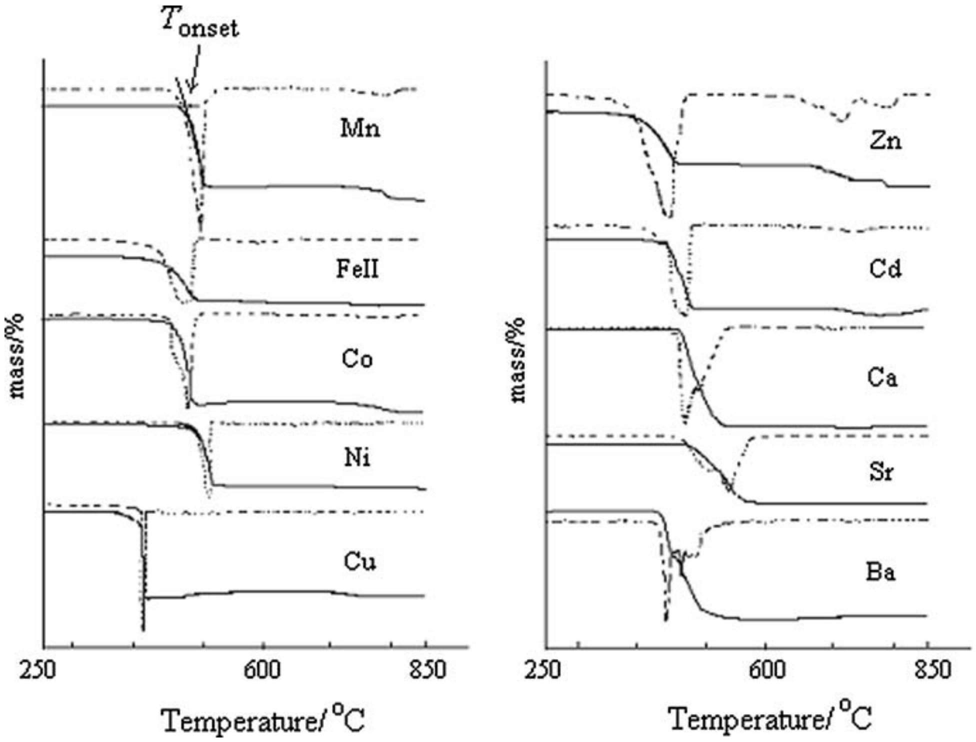


Fig. 1 TG/DTG curves of thermal decomposition of anhydrous bivalent methanesulfonates in dynamic Air atmosphere and heating rate of 20 K min^{-1}

Table 2 Thermal decomposition data of anhydrous bivalent $M(CH_3SO_3)_2$ in dynamic air atmosphere in the temperature range 250–850 °C

Anhydrous methanesulfonates	T_{onset}/°C	Residue mass fraction/%		Final residues and color characteristic of them	
		Found	Calcd.		
$Mn(CH_3SO_3)_2$	498	28.08	27.45	Mn_2O_3	Black
$Fe(CH_3SO_3)_2$	439	25.72	25.10	Fe_2O_3	Red
$Co(CH_3SO_3)_2$	452	26.34	25.11	Co_3O_4	Black
$Ni(CH_3SO_3)_2$	483	25.67	23.42	NiO	Green
$Cu(CH_3SO_3)_2$	412	24.11	24.43	CuO	Black
$Zn(CH_3SO_3)_2$	408	25.55	24.87	ZnO	White
$Cd(CH_3SO_3)_2$	446	39.57	38.10	CdO	White
$Mg(CH_3SO_3)_2$	476	21.85	22.03	$MgSO_4$ and MgO	White
$Ca(CH_3SO_3)_2$	474	41.87	41.74	$CaSO_4$ and CaO	White
$Sr(CH_3SO_3)_2$	486	54.93	54.69	$SrSO_4$	Hoar
$Ba(CH_3SO_3)_2$	436	68.73	71.26	$BaSO_4$	White

The samples were prepared as KBr diluted pellets in the solid-state.

X-ray powder diffraction patterns were obtained with a D/max-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

Thermal stability of anhydrous bivalent methanesulfonates

The TG/DTG curves of thermal decomposition of dehydrated or anhydrous bivalent transition metal and alkali earth metal methanesulfonates in dynamic Air atmosphere at 250–850 °C were shown in Fig. 1. After dehydration, anhydrous methanesulfonates keep stable for a rather wide range. Then methanesulfonates decompose sharply and rapidly to yield pyrolysis residues. T_{onset}, initial decomposition temperature represents relative thermal stability of methanesulfonates. From Table 1, all onsets of mass loss are above 400 °C, which shows the thermal stability of methanesulfonates is better. The onset of mass loss in TG increases in the series: Zn < Cu < Ba < Fe < Cd < Co < Ca < Mg < Ni < Sr < Mn. The pyrolysis products are classified into three types: metal oxide, sulphate and the complex of metal oxide and sulphate, shown in Table 1. The characteristic of them is discussed separately in the following way.

Thermal decomposition products of anhydrous bivalent transition metal methanesulfonates

For transition metal methanesulfonates, Charbonnier [8] has ever investigated that the final products of thermal decomposition are sulfides or metal substance in nitrogen atmosphere. In this paper, the residues at 850 °C are only metal oxides in air atmosphere and their calculated values approximated to their respective measured values, shown in Table 2. But definite experimental supports have been still lacking. In order to confirm whether the residuals are metal oxides, the infrared spectra of their thermal decomposition products at 850 °C are shown in Fig. 2. As can be seen from Fig. 2, there are not stretching vibration of O=S=O, but only characteristic peaks of M–O exist in the range 700–400 cm^{-1} clearly.

The following problem is to ascertain which oxidation states they are for transition metal exhibiting different valence. X-ray diffraction was therefore used in order to characterize the encountered phase at the end of the TG experiments. The comparison of the XRD spectrum of the pyrolysis product at 850 °C with standard spectrum was

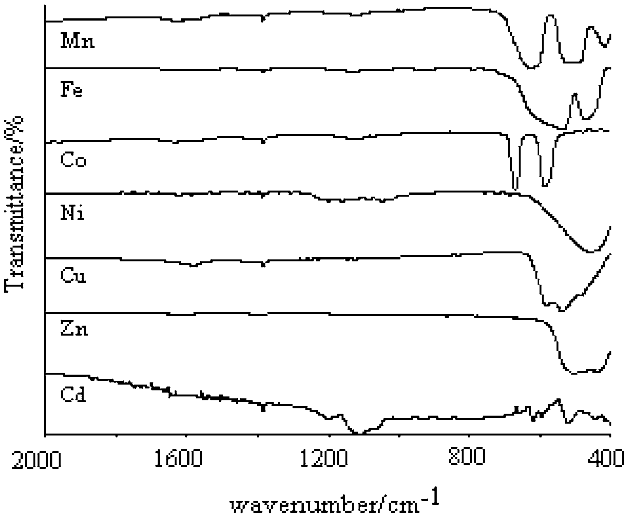
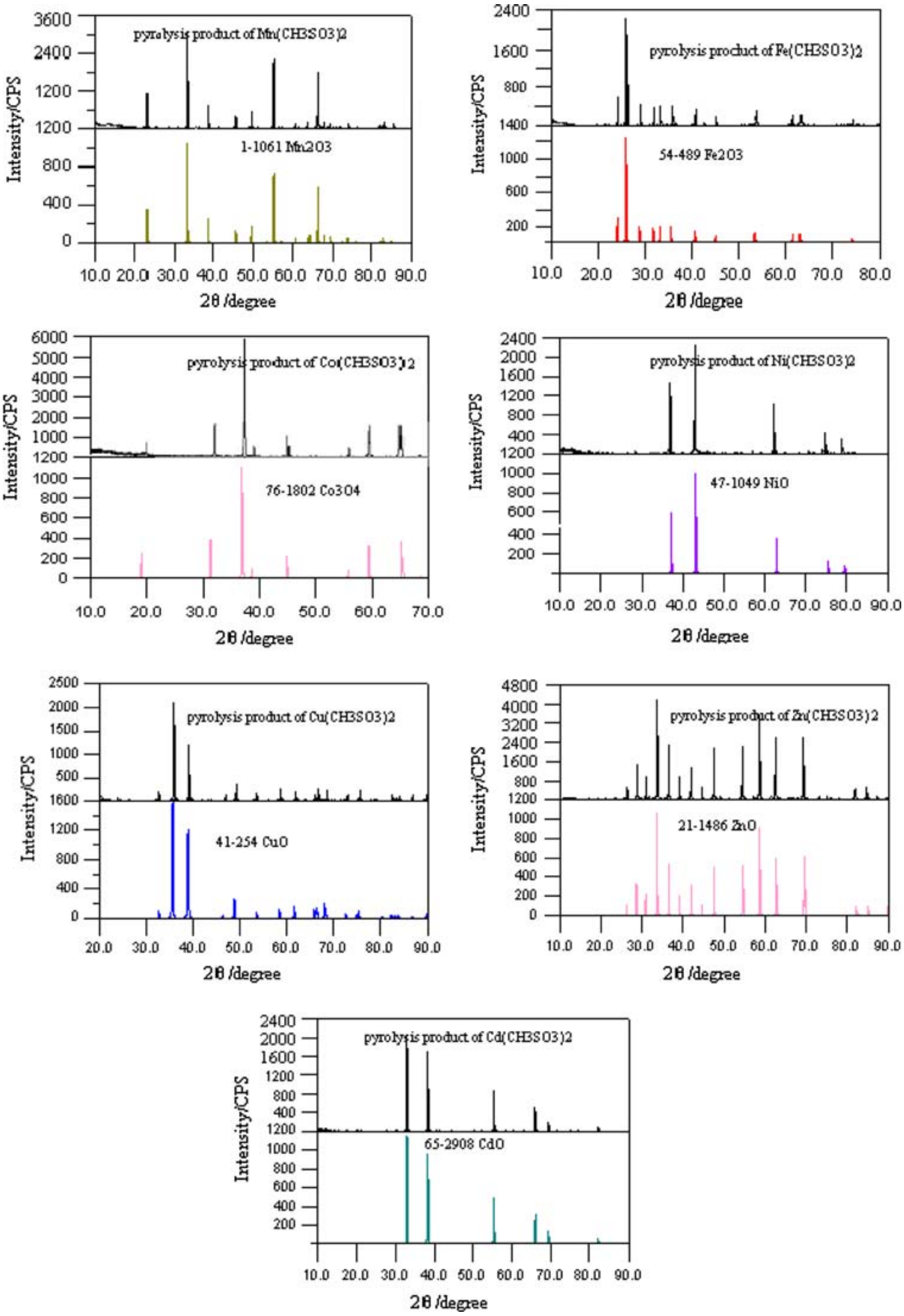


Fig. 2 IR spectra of thermal decomposition products at 850 °C of dehydrated bivalent transition metal methanesulfonates

shown in Fig. 3. The XRD spectrum clearly shows the correctness of the result identified by TG analysis in Table 2. In addition, through color characteristic of residuals, we can also conclude the final thermal decomposition product of ferrous methanesulfonate is red Fe_2O_3 (FeO and Fe_3O_4 are all black), that of nickel methanesulfonate is green NiO (Ni_2O_3 is black) and that of copper methanesulfonate is black CuO (Cu_2O is red). As to zinc, manganese and cadmium methanesulfonates, the final thermal decomposition residues of them are their general oxides, i.e. ZnO, Mn_2O_3 and CdO, respectively. Hence, the final products of thermal decomposition of transition metal methanesulfonates at 850 °C are believed to be corresponding metal oxides.

Fig. 3 XRD match results of pyrolysis products at 850 °C of dehydrated bivalent transition metal methanesulfonates with standard spectra



Thermal decomposition products of anhydrous bivalent alkali earth metal methanesulfonates

In the title compounds, alkali earth metal methanesulfonates are special group for their pyrolysis products at 850 °C are not single. The residuals of anhydrous strontium and barium methanesulfonates are sulphates, while those of anhydrous magnesium and calcium methanesulfonates are mixtures of sulphate and oxide. The characterizations were as follows:

The infrared spectra of their thermal decomposition products at 850 °C are shown in Fig. 4. In Fig. 4, the main absorption peaks of the residues of $Sr(CH_3SO_3)_2$ and $Ba(CH_3SO_3)_2$ were approximately the same. The strong absorption in the range 1234–1085 cm^{-1} are caused by stretch vibration of O=S=O, and absorption in the range 1027–983 cm^{-1} should be ascribed to stretch vibration of O–S–O in SO_4^{2-} groups. Furthermore, mediate strong absorption in the range 678–504 cm^{-1} should be the contribution of bend vibration of S–O or S=O. Therefore, the decomposition residue of them should contain SO_4^{2-} groups. There is great difference between the theoretical value and experimental value if the thermal decomposition products of $Mg(CH_3SO_3)_2$ and $Ca(CH_3SO_3)_2$ are assumed as sulphate or oxide. Both vibrations of O=S=O, O–S–O and M–O are exist in the IR spectrum of pyrolysis product of $Mg(CH_3SO_3)_2$. The vibrations of O=S=O and O–S–O are not obvious in the IR spectrum of pyrolysis product of $Ca(CH_3SO_3)_2$. It cannot confirm the residual only from IR characterization. Therefore, X-ray diffraction technique was used.

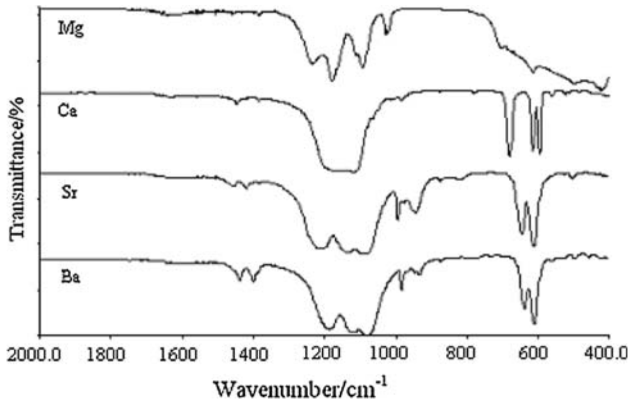
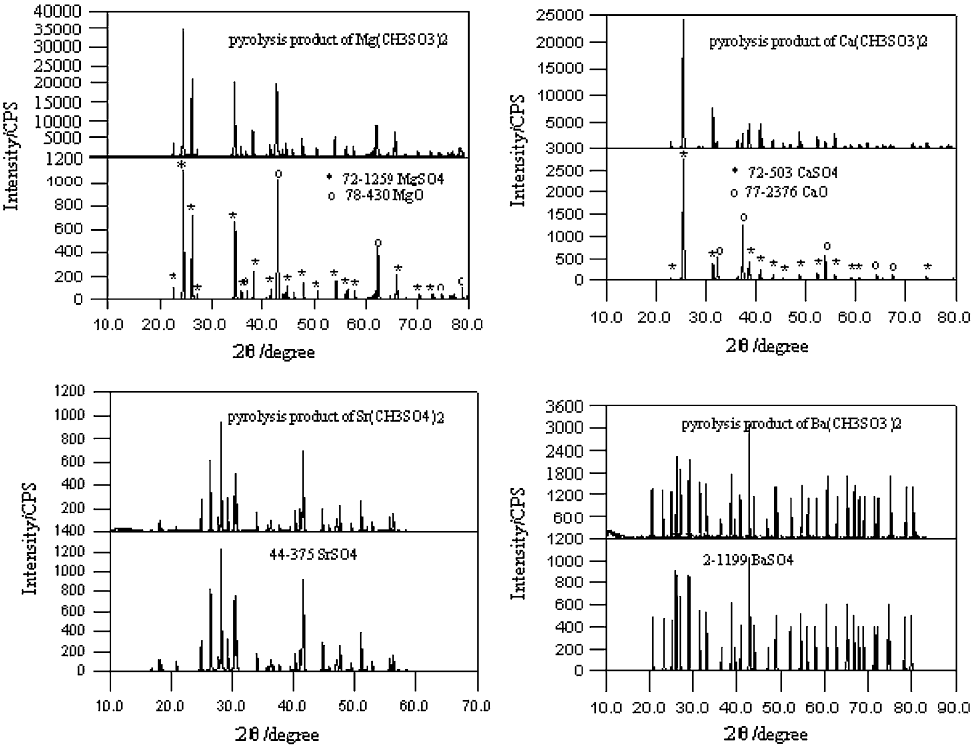


Fig. 4 The IR spectra of thermal decomposition products at 850 °C of anhydrous Mg, Ca, Sr, Ba methanesulfonates

The pyrolysis residues of $Mg(CH_3SO_3)_2$, $Ca(CH_3SO_3)_2$, $Sr(CH_3SO_3)_2$ and $Ba(CH_3SO_3)_2$ at 850 °C were subjected to XRD studies (Fig. 5). Through comparing the spectra of the pyrolysis residues at 850 °C with standard spectra, it shows clearly the final products of $Sr(CH_3SO_3)_2$ and $Ba(CH_3SO_3)_2$ were sulphates, while thermal decomposition products of $Mg(CH_3SO_3)_2$ and $Ca(CH_3SO_3)_2$ were mixtures of sulphate and oxide rather than simple sulphate. This fact provides further support for the analytical results from TG and IR. It can be calculated from TG and XRD data that the mass content of $MgSO_4$ in pyrolysis product is

Fig. 5 XRD match results of pyrolysis products at 850 °C of anhydrous Mg, Ca, Sr, Ba methanesulfonates with standard spectra



20% and $CaSO_4$ in pyrolysis product is 50%. The others were their corresponding metal oxides, respectively.

Conclusions

The thermal stability and pyrolysis products at 850 °C of some representative dehydrated or anhydrous bivalent transition metal (Mn, Fe, Co, Ni, Cu, Zn, Cd) and alkali rare metal (Mg, Ca, Sr, Ba) methanesulfonates in dynamic Air have been studied in this paper. The initial decomposition temperatures of them are above 400 °C. The decomposition residues are classified into three types: metal oxide, sulphate and the complex of metal oxide and sulphate. The type of the pyrolysis products of the title samples prepared depends on the metal ion in the parent material.

References

1. Wang M, Wang ZC, Sun ZL, Jiang H. Reaction-controlled recovery of the copper(II) methanesulfonate catalyst for esterification. React Kinet Catal Lett. 2005;84:223–8.
2. Wang M, Wang ZC, Sun ZL, Jiang H. Synthesis and characterization of transition metal methanesulfonates and their catalytic behavior in Biginelli reactions. Transition Met Chem. 2005;30:792–6.
3. Wang M, Jiang H, Wang ZC. Biginelli condensation of aliphatic aldehydes catalysed by zinc methanesulfonate. J Chem Res. 2005;11:691–3.
4. Wang M, Gong H, Jiang H, Wang ZC. Acetic acid-assisted copper methanesulfonate catalyst for chemoselective conversion of aldehydes to acylals. Synth Commun. 2006;36:1953–60.
5. Wang M, Song ZG, Jiang H, Gong H. Tetrahydropyranylation of alcohols and phenols using the synergistic catalyst system, copper (II) chloride-acetic acid. Monatsh Chem. 2007;138:599–602.
6. Aricó EM, Zinner LB, Apostolidis C, Dornberger E, Kanellakopulos B, Rebizant J. Structures of the anhydrous Yb(III) and the hydrated Ce(III), Sm(III) and Tb(III) methanesulfonates. J Alloys Compd. 1997;249:111–5.
7. Aricó EM, Zinner LB, Kanellakopulos B, Dornberger E, Rebizant J, Apostolidis C. Structure and properties of hydrated La(III), Nd(III) and Er(III) methanesulfonates. J Alloys Compd. 2001;39:323–4.
8. Charbonnier F. Thermal behavior of some compounds of methanesulfonic acid with transition metals. Thermochim Acta. 1979;33:31–9.
9. Tian J, Jiang H, Gong H, Sun Z. Research of thermal decomposition of hydrated methanesulfonates. J Therm Anal Cal. 2004;77:825–31.
10. Moura MFV, Matos JR, Farias RF. Thermal degradation study of gadolinium and lutetium methanesulfonates. Thermochim Acta. 2004;414:159–66.
11. Wang M, Jiang H, Wang ZC. Dehydration studies of Co(II), Cu(II) and Zn(II) methanesulfonates. J Therm Anal Cal. 2006;85:751–4.