Journal of Thermal Analysis and Calorimetry, Vol. 60 (2000) 219–227

REDUCTION AND OXIDATION OF SIMPLE OXOCUPRATES

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Abstract

Oxidation-reduction reactions were studied for the following oxocuprates: LiCuO, Li_2CuO_2, $SrCu_2O_2$, Sr_2CuO_3, $SrCuO_2$, $BaCu_2O_2$, $BaCuO_2$, $LaCuO_2$, La_2CuO_4, Ca_2CuO_3 and Bi_2CuO_4. Transformation schemes have been proposed for the anionic sub-lattices of these salts and the effect of cations on the properties of the anionic sub-lattices in oxidation-reduction reactions was determined.

Keywords: oxidation-reduction reactions, oxocuprates, TG-DTG-DTA

Introduction

The work has been devoted to investigation of fundamental chemical properties of simple oxocuprates. Scientific centers throughout the world are working on possibilities of increasing the critical temperature and on new methods of synthesis. Little attention has been paid to simple oxocuprates, which have been the precursors of superconducting systems, thus the study of chemical properties of simple oxocuprates is extremely important for the knowledge of chemistry of the superconducting systems. Nowadays copper compounds are being studied very intensely because of their application in high-temperature superconductors. Their structures are determined and conditions of their syntheses are established. However, there are very few comprehensive studies on their chemical properties, in particular, on their reactivity toward oxidizing and reducing agents, such as O_2 and H_2, or on the manner in which cations influence the reactivity of anionic sub-lattices, or finally – what is the effect of anionic sublattice in systems with identical cations. Copper forms oxo-compounds at three oxidation states. Simple species of copper are presented in the Górski's classification system in Table 1.

The aim of the work was to find relationships between the different kinds of copper oxocompounds in their redox reactions. The studies were based on compounds comprising the following kinds of oxocuprate species:

$$CuO_3^{3-}, CuO_3^{4-}, CuO_2^{2-}, CuO, CuO_2^{3-}, CuO^{-} \text{ and } Cu_2O.$$

1418–2874/2000/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Table 1 Simple species of copper in the Górski's classification system

e_z	Copper and oxocuprates			
8		CuO_4^{6-}		
7				
6	CuO_3^{3-}	CuO_3^{4-}		
5		$Cu_2O_5^{6-}$		
4	CuO_2^{6-}	CuO_2^{2-}	CuO_2^{3-}	
3		$Cu_2O_3^{2-}$	$Cu_2O_3^{4-}$	
2		CuO	CuO^-	
1			Cu_2O	
0	Cu^{3+}	Cu^{2-}	Cu^+	Cu°
e_v	8	9	10	11
G_{ox}	+3	+2	+1	0

Experimental

The following compounds were synthesized: LiCuO [1], Li_2CuO_2 [2], $SrCu_2O_2$ [3], Sr_2CuO_3 [4], $SrCuO_2$ [5], $BaCu_2O_2$, $BaCuO_2$ [6], $LaCuO_2$, La_2CuO_4 [7], Ca_2CuO_3 [5] and Bi_2CuO_4 [8]. The syntheses were carried out as solid state reactions in tubular furnace in air or nitrogen atmospheres. Raw materials used for the syntheses were: Li_2O obtained by decomposition of commercial 90% Li_2O_2 (Aldrich), $CaCO_3$ of purity grade 98% (BDH), BaO of purity 97% (Aldrich), SrO obtained by decomposition of SrO_2 (Aldrich), La_2O_3 purum (Fluka AG), and Bi_2O_3 from BiO(OH) decomposition (Chemapol Praga). Conditions of the syntheses are listed in Table 2.

Table 2 Conditions of the syntheses of oxocuprates

Raw material	Molar ratio	Temp./°C	Reac. time/h	Atmosphere	Product
Li_2O+Cu_2O	1:1	650	3	N_2	LiCuO
$LiOH{\cdot}H_2O$+CuO	2:1	650	3	air	Li_2CuO_2
SrO+Cu_2O	1:1	750	12	N_2	$SrCu_2O_2$
SrO+CuO	1:1	900	5	air	$SrCuO_2$
SrO+CuO	2:1	900	5	air	Sr_2CuO_3
BaO+Cu_2O	1:1	800	5	N_2	$BaCu_2O_2$
BaO+CuO	1:1	950	3	air	$BaCuO_2$
La_2O_3+Cu_2O	1:1	950	20	N_2	$LaCuO_2$
La_2O_3+CuO	1:1	900	15	air	La_2CuO_4
$CaCO_3$+CuO	2:1	900	16	air	Ca_2CuO_3
Bi_2O_3+CuO	1:1	750	2	air	$Cu(BiO_2)_2$

For the sake of clarity the work has been divided into two parts. The first part has been devoted to reduction, and the second to oxidation of the obtained oxocuprates. For space-saving reasons only a limited number of the DTA curves and graphical results of the complex thermal analysis have been included.

The reactions of reduction were studied in a measuring setup that enabled to record thermal effects occurring as a functions of temperature. The reducing agent was gaseous hydrogen diluted with nitrogen. The thermal effects were recorded by means of a microprocessor device. All reductions were carried out at a constant rate of temperature increase of 4.4°C min^{-1} under constant flow rate of hydrogen (2 $\mathrm{dm}^3\ \mathrm{min}^{-1}$) and nitrogen (0.8 $\mathrm{dm}^3\ \mathrm{min}^{-1}$).

In the second part of the work the object of the studies were reactions of oxidation of simple oxocuprates(I). The studies were based on complex thermal analysis with the use of derivatograph Q 1500D (MOM, Budapest) and an X-ray phase analysis with the use of HZG-3 Tur device (Germany) with CuK_α radiation. The samples were heated in air atmosphere.

Results and discussion

Reduction reactions

The following copper(II) compounds were subjected to reduction with hydrogen: CuO, Li_2CuO_2, $SrCuO_2$, $BaCuO_2$, and $(LaO)_2CuO_2$.

The DTA curve obtained in reduction of CuO exhibits two effects with maximums at 196 and 312°C (Fig. 1a). The former is due to the reduction of CuO to Cu_2O in reaction:

$$2CuO + H_2 \rightarrow Cu_2O + H_2O$$

and the latter is connected with reaction:

$$Cu_2O + H_2 \rightarrow 2Cu + H_2O$$

Copper(II) oxide is reduced at the lowest temperature. Anionic sub-lattices containing copper(II) are reduced at much higher temperatures.

The DTA curve of Li_2CuO_2 (Fig. 1c) is featured by two partly superposed effects with maximums at 409 and 440°C. At the first step the initial compound is reduced to LiCuO:

$$2Li_2CuO_2 + H_2 \rightarrow 2LiCuO + Li_2O + H_2O$$

At the second step, proceeding at a higher temperature, LiCuO is reduced to copper metal:

$$2LiCuO + H_2 \rightarrow 2Cu + Li_2O + H_2O$$

A similar, two-step reduction is observed for $BaCuO_2$ (Fig. 1d). At the first step, with a maximum on DTA curve at 370°C, the compound is reduced to $BaCu_2O_2$:

$$2BaCuO_2 + H_2 \rightarrow BaCu_2O_2 + H_2O + BaO$$

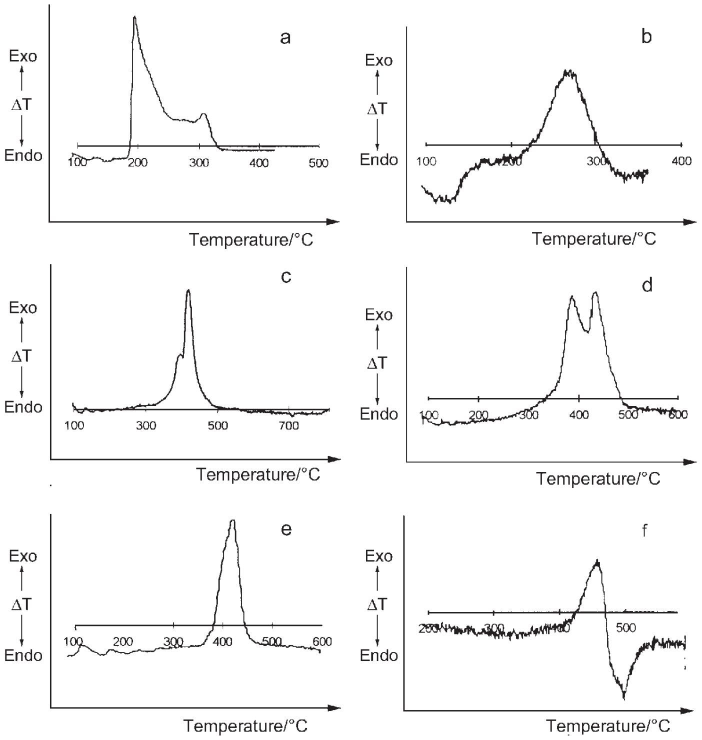

Fig. 1 DTA curves of reduction reactions; a – CuO; b – Cu_2O; c – Li_2CuO_2; d – $BaCuO_2$; e – LiCuO; f – $SrCu_2O_2$

At the second step, with a maximum at 440°C, the cuprate(I) is reduced to copper metal:

$$2BaCu_2O_2 + H_2 \rightarrow BaO + 2Cu + H_2O$$

The reduction of $SrCuO_2$ proceeds at temperature range 440–530°C, in a single step reaction leading to formation of free copper.

$$SrCuO_2 + H_2 \rightarrow SrO + Cu + H_2O$$

A two-stage reaction is also observed in reduction of $(LaO)_2CuO_2$. In the first stage, at 300°C, a Cu(I) compound is formed:

$$2La_2CuO_4 + H_2 \rightarrow 2LaCuO_2 + La_2O_3 + H_2O$$

The intermediate compound formed is further reduced at 520°C to give Cu metal:

$$2LaCuO_2 + H_2 \rightarrow La_2O_3 + 2Cu + H_2O$$

The reduction of two copper compounds containing the anionic sub-lattice of CuO_3^{4-} namely Ca_2CuO_3 and Sr_2CuO_3 proceeds in a single step reaction leading to formation of copper metal. The calcium salt is reduced within 400–500°C with a maximum at 430°C.

$$Ca_2CuO_3 + H_2 \rightarrow 2CaO + Cu + H_2O$$

and the strontium salt is reduced at 440–495°C:

$$Sr_2CuO_3 + H_2 \rightarrow 2SrO + Cu + H_2O$$

$Cu(BiO_2)_2$, which comprises copper in the form of Cu^{2+} cations, is reduced by hydrogen in a process with a maximum on DTA curve at 514°C to give free metals:

$$Cu(BiO_2)_2 + 4H_2 \rightarrow 2Bi + Cu + 4H_2O$$

Reduction of copper(I) oxo-compounds by means of hydrogen proceeds at higher temperatures. Copper(II) oxide is reduced by hydrogen with a maximum effect at 312°C. An oxide obtained from Cu(I) was reduced in a single step reaction with a maximum at 267°C (Fig. 1b), and the one obtained by thermal decomposition of CuO at 990°C was reduced at 340°C. These examples show that the reactivity of Cu_2O depends on the conditions of its synthesis.

The reduction of LiCuO proceeds according to the following reaction, with a maximum at 430°C (Fig. 1e). The temperature, at which this reaction is effected, is close to the temperature of reduction of this compound when obtained as an intermediate product in the reduction of Li_2CuO_2.

$SrCu_2O_2$ (Fig. 1f) is reduced to copper metal in the following reaction:

$$SrCu_2O_2 + H_2 \rightarrow SrO + 2Cu + H_2O$$

The maximum of DTA effect due to this reaction is observed at 460°C, which is close to a maximum temperature of $SrCuO_2$ reduction. This is the reason why $SrCu_2O_2$ is not formed in the reduction of $SrCuO_2$.

$BaCu_2O_2$ is reduced by hydrogen in the following reaction having a maximum on DTA curve at 420°C:

$$BaCu_2O_2 + H_2 \rightarrow BaO + 2Cu + H_2O$$

The intermediate compound formed in the reduction of $BaCuO_2$ is reduced by hydrogen with a maximum on the DTA curve at 440°C.

In reduction of $LaCuO_2$ the effect on DTA curve with a maximum at 485°C corresponds to the reaction:

$$2LaCuO_2 + H_2 \rightarrow La_2O_2 + 2Cu + H_2O$$

The effect on the DTA curve occurs at a lower temperature than that observed in reduction of $LaCuO_2$ obtained as an intermediate product in reduction of $(LaO)_2CuO_2$.

Oxidation reactions

All copper(I) compounds are oxidized by O_2.

Thermogravimetric curves of LiCuO oxidation in the air are shown in Fig. 2. The compound is oxidized in the temperature range of 180–440°C with a maximum

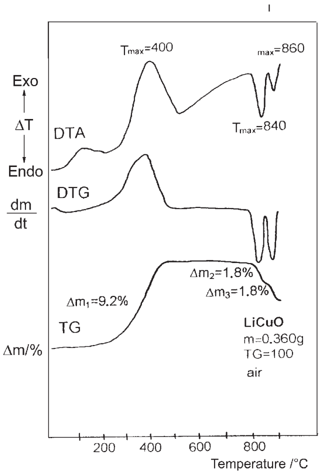

Fig. 2 TG, DTG, DTA curves of oxidation reaction of LiCuO

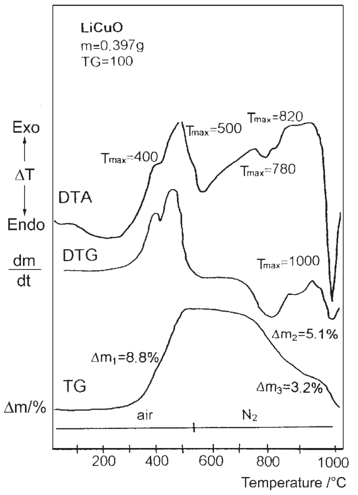

Fig. 3 TG, DTG, DTA curves of oxidation reaction of LiCuO (air and N_2)

rate at 390°C and strong endothermic effect. The products contained Li_2CuO_2 and CuO. The observed increase in mass of 9.2% correspomds to the following stoichiometry:

$$2LiCuO + 1/2O_2 \rightarrow Li_2CuO_2 + CuO$$

The oxidation products are stable up to 820°C. At higher temperatures two endothermic effects are observed, with maximums at 840 and 880°C. In either case the loss in mass was 1.8%. Analysis of the products obtained >880°C revealed the presence of Li_2CuO_2 and $LiCu_3O_3$, and the absence of CuO. Evidently it is due to the following reaction:

$$4Li_2CuO_2 + 4CuO \rightarrow 2Li_2CuO_2 + 2LiCu_3O_3 + Li_2O + 1/2O_2$$

At temperatures above 980°C the liberation of oxygen continues and the products react with each other to give LiCuO. The process is confirmed by the thermogravimetric curve shown in Fig. 3. In this process a LiCuO sample was oxidized by heating in the air up to 500°C and heating was then continued in nitrogen atmosphere. Two effects of mass loss observed on heating in the air join together and the effects are shifted toward lower temperatures. Maximums on the DTA curve appear at 780 and 820°C. In nitrogen atmosphere the reaction of LiCuO formation begins as early as at 900°C and the sample mass comes back to its initial value.

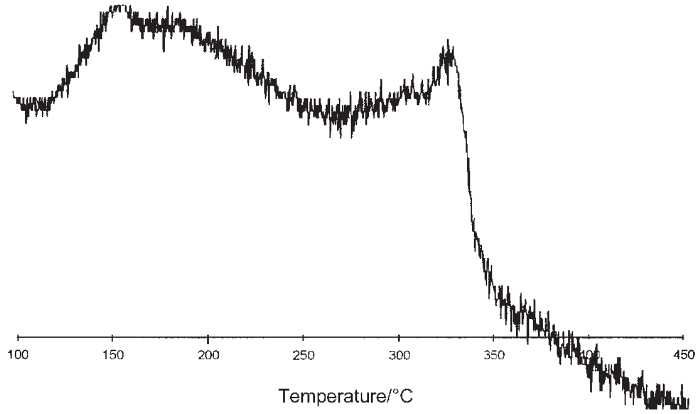

Fig. 4 DTA curves of oxidation reaction of LiCuO (O_2)

LiCuO was also oxidized in a stream of gaseous oxygen, with recording of the DTA curve (Fig. 4). The oxidation started at 200°C and attained a maximum at 300°C. The product mixture contained, besides CuO and Li_2CuO_2, also a copper(III) compound, namely $Li_3Cu_2O_4$. The oxidation in pure oxygen proceeded according to the following stoichiometry:

$$10LiCuO + 3O_2 \rightarrow 2Li_2CuO_2 + 2Li_3Cu_2O_4 + 4CuO$$

Thermogravimetric analysis of $BaCu_2O_2$ (Fig. 5) has shown that the oxidation proceeds in the temperature range 340–500°C, and the maximum of the exothermic effect is attained at 460°C. The products obtained in the first stage of the reaction contained copper(II) compounds: $Ba_2Cu_3O_6$ and CuO. The reaction proceeded at 620°C according to the following equation:

$$4BaCu_2O_2 + 3O_2 \rightarrow 2Ba_2Cu_3O_6 + 2CuO$$

The resulting system was thermally stable up to 860°C, at which a 2.3% loss in mass began and had its end at 880°C. The reaction had an endothermic effect, with a maximum at 820°C, due to the reduction of Cu(III).

$$2Ba_2Cu_3O_6 \rightarrow 4BaCuO_2 + 2CuO + O_2$$

A following mass loss begins at 910°C and ends at 1000°C.

$$2CuO \rightarrow Cu_2O + 1/2O_2.$$

Investigation of the thermal effects occurring during oxidation of $BaCu_2O_2$ has shown that the reaction has the highest rate at 350°C, and the products have the composition $BaCuO_{2+x}$>

$$BaCu_2O_2 + xO_2 \rightarrow BaCuO_{2+x/2} + CuO$$

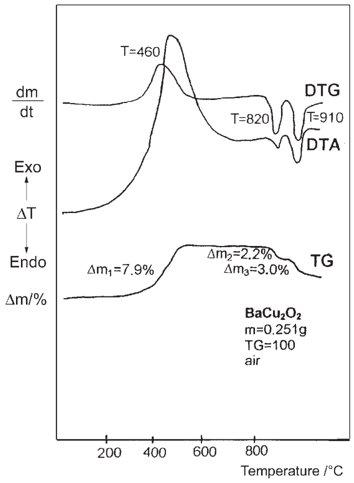

Fig. 5 TG, DTG, DTA curves of oxidation reaction of $BaCu_2O_2$

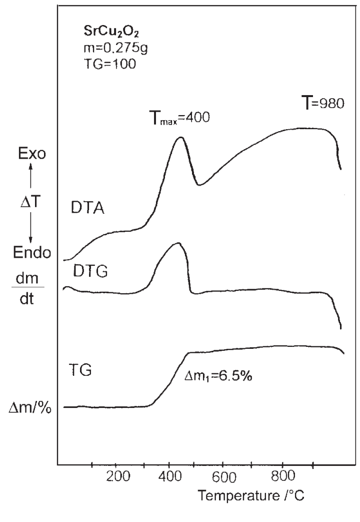

Fig. 6 TG, DTG, DTA curves of oxidation reaction of $SrCu_2O_2$

The thermogravimetric analysis of $LaCuO_2$ has shown that the oxidation proceeds within 340–580°C and the product obtained is stable up to 1000°C. The results obtained, along with those of X-ray pwoder diffraction analysis have shown that the reaction proceeds with the following stoichiometry:

$$2LaCuO_2 + 1/2O_2 \rightarrow La_2CuO_4 + CuO$$

The oxidation of $SrCu_2O_2$ (Fig. 6) has shown that the reaction proceeds in a single step within 340–500°C. The results of the X-ray phase analysis have proved that the oxidation products are limited to $SrCuO_2$ and CuO. Above 980°C a loss in mass is observed. The X-ray phase analysis of a sample heated in the air up to that temperature and then rapidly cooled in nitrogen has revealed the presence of $SrCuO_2$ as the main phase, and certain amounts of Sr_2CuO_3 and $SrCu_2O_2$.

The oxidation of $SrCu_2O_2$ by pure oxygen is effected in a temperature range 300–600°C. The maximum of the thermal effect is observed at 320°C. The oxidation products of the reaction are: $Sr_{1.75}Cu_3O_{5.13}$, $SrCu_2O_3$ and SrO.

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