

## Synthesis of Nanosized Oxides by Thermal Decomposition of Citrate Precursors

I.V. Romanova<sup>1</sup>, I.I. Farbun<sup>1</sup>, S.A. Kirillov<sup>1,2,\*</sup>

<sup>1</sup> Institute for Sorption and Problems of Endoecology, 13, Gen. Naumov St., 03164 Kyiv, Ukraine

<sup>2</sup> Joint Department of Electrochemical Energy Systems, 38A, Vernadsky Ave., 03142 Kyiv, Ukraine

(Received 20 May 2013; published online 31 August 2013)

The paper describes the citric acid aided synthesis of single and mixed nanosized oxides of transition metals (Zn, Cu, Co, Ni, Mn, Ce). Thermal analysis is used for determining the composition of precursors and intermediates formed in the process of their pyrolysis and for finding minimal temperatures of the formation of oxide. All samples studied are found to be nanoporous materials with predominant mesoporosity. The greatest surface area is obtained for samples with metal to citric acid ratio as 1 : 2. Overlooking the results of porosity studies one can reach a conclusion regarding the optimal composition of the precursors for obtaining each of target materials of the best quality.

**Keywords:** Citrate precursors, Nanoporous materials.

PACS numbers: 82.33.Pt

### 1. INTRODUCTION

Polybasic hydroxy and amino carboxylic acid routes offer great advantages for the synthesis of oxide nanomaterials with great surface area and porosity, viz., high degree of reproducibility, potential for large-scale production and low cost. During the past 10 years we have synthesized more than 100 individual and mixed oxides of transition metals, viz., Zn, Cu, Co, Ni, Mn and Ce [1-5]. Materials obtained have been used as catalysts and electrochemical materials. A big problem for further applications of these oxides in any field is the agglomeration of particles during the process of thermal decomposition.

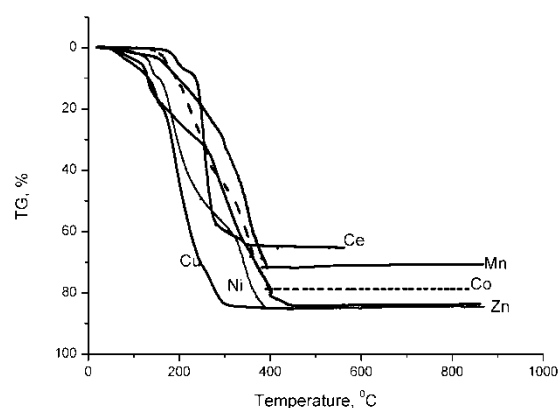
This study is devoted to the effect of citrate precursors (nature of metal ions and the molar ratio of the initial components) on the thermal decomposition and pore structure of individual oxides of zinc, copper, cobalt, nickel, manganese and cerium. Also, we describe the same mixed oxides successfully tested in catalysis. The thermal decomposition of initial citrate precursors is analyzed using DTA, IR, XRD, SEM, TEM methods and porosity measurements.

### 2. RESULTS AND DISCUSSION

Results of chemical and thermal analyzes of citrate precursors show that the interaction of transition metal nitrates with the equimolar amount of citric acid leads to the formation of hydrated metal citrates of the  $\text{MeC}_6\text{H}_6\text{O}_7 \cdot n\text{H}_2\text{O}$  composition, where  $n = 1-3$ , and in the case of double excess of citric acid,  $\text{Me}(\text{C}_6\text{H}_7\text{O}_7)_2 \cdot n\text{H}_2\text{O}$  compounds are formed, where  $n = 1-5$ . Only manganese forms the equimolar compounds at all initial molar ratios of components. Thermal analysis has been used for determining the composition of the precursors and intermediates formed in the process of their pyrolysis and for finding the minimal temperature of the formation of oxide.

The thermal decomposition behavior of the precursors has been found to depend on the nature of

the metal (Fig. 1). Decomposition occurs by a multistep reaction as was described for Zn [4]. Heating amorphous precursors to 160 °C causes the loss of water accompanied with a small exothermic effect associated with the crystallization of anhydrous citrates. At further heating in the temperature range 160-230 °C, the transformation of citrate to aconitate should occur. The thermal decomposition of this compound leads to the formation of citraconate that is finally decomposed in the range of 300-450 °C giving metal oxides. It is accompanied by the consecutive burning of cyclic anhydrides formed by the destruction of citric acid. Unlike the precursor with the 1 : 2 metal to citric acid ratio, those having the 1 : 1 ratio demonstrate higher temperature of the formation of oxides. Summarizing the results of the thermal analysis, a conclusion can be drawn that the temperature of the complete decomposition and formation of metal oxides depend on the nature of metal.



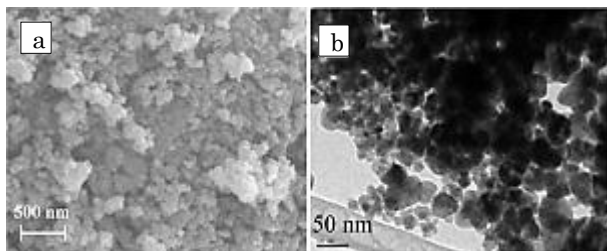
**Fig. 1** – TG plots for the citrate precursors of different metal oxides with the initial metal to citric acid ratio of 1 : 2

X-ray analysis of samples after the heat treatment indicates the formations of a single phase of metal

\* [kir@i.kiev.ua](mailto:kir@i.kiev.ua)

oxides in the case of Zn, Cu, Co, Ni and Ce. Heat treatment of the manganese citrate precursor at 400 °C leads to the formation of different compounds: for the 1 : 1 ratio,  $MnO_{1,36}$  (a mixture of 77,8 %  $Mn_3O_4$  и 22,2 %  $Mn_2O_3$ ), and for the 1 : 1 ratio,  $MnO_{1,352}$  (a mixture of 82,8 %  $Mn_3O_4$  и 17,2 %  $Mn_2O_3$ ).

The mean crystallite sizes ( $D_{Sch}$ , nm) have been calculated according to the line width method based on the Scherrer equation. For all samples values  $D_{Sch}$  do not exceed 30 nm. According to SEM data, metal oxide samples thermally treated at 400 °C consist of aggregates of < 100 nm size (Fig. 2a). TEM data reveal that the aggregates consist of particles of ~ 30 nm (Fig. 2b).



**Fig. 2** – SEM (a, 30,000 times magnification) and TEM (b, 200,000 times magnification) of ZnO samples thermally treated at 400 °C

All samples studied should be described as nanoporous materials with predominant mesoporosity. Their nitrogen adsorption-desorption isotherms, according to the IUPAC classification, belong to the II type with the hysteresis loop of the H3 type. An increase in the amount of citric acid does not cause changes in the type of the isotherms and hysteresis loops. All samples demonstrate small initial parts indicating an insignificant number of micropores in the samples. It has been also found that  $S_{sp.}$ , the specific surface area values increase upon heating to 400 °C

## REFERENCES

1. S.A. Kirillov, I.V. Romanova, I.A. Farbun, *New Carbon Based Materials for Electrochemical Energy Storage Systems* (Ed. I.V. Barsukov, C. Johnson, J. Doninger) (Kluwer: Dordrecht: 2006).
2. I.A. Farbun, I.V. Romanova, T.E. Terikovskaya, D.I. Dzanashvili, S.A. Kirillov, *Russ. J. Appl. Chem.* **80** No 11, 1773 (2007).
3. I.V. Romanova, I.A. Farbun, S.A. Khainakov, S.A. Kirillov,

and then become gradually smaller.

The greatest surface areas have been obtained for the samples with the metal to citric acid ratio of 1 : 2. This is true for both single and mixed oxides (Table 1). For all samples, the presence of micropores has been found.

**Table 1** – Porosity data for samples of metal oxides obtained from citrate precursors at initial component ratio 1 : 2.  $V$  – pore volume, MP – percent of micropores,  $r$  – mean pore radius

Sample	$S_{sp.}$ , m <sup>2</sup> /g	$V$ , cm <sup>3</sup> /g	MP, %	$r$ , nm
ZnO	58,06	0,09	8,1	2,0
CuO	5,0	0,02	0	9,3
NiO	14,6	0,06	0	4,75
CoO	3,94	0,08	0	1,05
MnO <sub>n</sub>	44,36	0,22	0	3,8
CeO <sub>2</sub>	40,51	0,09	11,0	1,9
CuO-CeO <sub>2</sub>	51,13	0,07	16,4	1,9
MnO <sub>n</sub> -CeO <sub>2</sub>	113,0	0,13	19,62	1,9

## 3. CONCLUSION

Overviewing the results of porosity studies one can reach a conclusion regarding the optimal composition of the precursors for obtaining the each of target materials of the best quality. In particular, for all samples the mixtures containing two moles of citric acid per one mole of metal are optimal and give the nanosized target oxide having the greatest surface area, the smallest pores and the greatest micropore fraction.

Mixed oxides of various compositions have been tested in catalytic studies. In the reaction of oxidation of CO, the best catalytic activity is found for CuO-CeO<sub>2</sub> catalysts. MnO<sub>x</sub> has showed the highest activity for ethyl acetate and toluene oxidation, while MnO<sub>n</sub>-CeO<sub>2</sub> has been more active for ethanol oxidation.

V.A. Zazhigalov *Reports of Academy of Science of Ukraine* **No 10**, 153 (2008).

4. I.A. Farbun, I.V. Romanova, S.A. Kirillov *J. Sol-Gel Sci. Tech.*, DOI: 10.1007/s10971-013-3024-7 (2013).
5. A.V. Potapenko, S.I. Chernukhin, I.V. Romanova, S.A. Kirillov, *Chemistry, Physics and Technology of Surface* **2** No 2, 175 (2011). [in Russian].