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THERMAL BEHAVIOUR OF SOME Al(III)-Mg(II) POLYNUCLEAR COORDINATION COMPOUNDS WITH POLYCARBOXYLIC ACID ANIONS AS LIGANDS, PRECURSORS OF ALUMINATES

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A TG, DTG and DTA study of three polynuclear coordination compounds, containing Al(III)-Mg(II), namely $(NH_4)_4[Al_2Mg(C_4O_5H_4)_4(OH)_4]\cdot 2H_2O$, $(NH_4)_4[MgAl_2(C_4H_4O_6)_4(OH)_4]\cdot 3H_2O$ and $(NH_4)_2[Al_2Mg(C_6O_7H_{11})_5(OH)_5]\cdot 3H_2O$, has been reported together with the associated thermal decomposition mechanism rationalized in terms of intermediate products. As decomposition end-product, magnesium-aluminum spinel is obtained. The values of $MgAl_2O_4$ mean crystallite size depend on the anionic ligand contained by the precursor compound, varying in the order: malate (143 Å)<gluconate (165 Å)<tartarate (180 Å).

Keywords: *magnesium-aluminum complexes, magnesium-aluminum spinel, thermal analysis*

Introduction

Magnesium-aluminum spinel ($MgAl_2O_4$) is used in a wide range of applications, such as refractory materials, humidity and infrared sensors, transparent windows, catalysts and as armour materials [1–10].

Various chemical routes have been adopted for synthesis single phase magnesium-aluminium spinels, among which we mention solid state methods namely traditional [11–14] and mechanochemical [15] ones, and wet chemical approaches like coprecipitation [16], microemulsion [17], different sol-gel variants [18–23] and autocombustion procedures (such as urea-nitrate [24, 25] and citrate-nitrate [26]).

Although in the last decade the use of polynuclear compounds as sources of oxides with various structures (spinelic, garnet, hexagonal, perovskitic ones), has expanded [27–29], no reports concerning the synthesis of magnesium-aluminum spinel through this method is mentioned till now.

The present paper reports the synthesis of magnesium-aluminum spinel starting from three polynuclear coordination compounds, containing as ligands malic, tartaric and gluconic acids anions. The influence of the complexing agent on the thermal behavior of the precursors and implicit mixed oxides properties is emphasized.

Experimental

The synthesis of the polynuclear compounds represents a version of the one used by Melson and Pickering [30]. From the reaction medium, a solution containing metal nitrates and polyhydrocarboxylic acid, in a ratio Al(III):Mg(II):polycarboxylic acid of 2:1:4 (malic and tartaric acids) and 2:1:8 (gluconic acid), the polynuclear coordination compounds were separated by extraction with ethanol. A complete precipitation required 24 h, time interval in which repeated adjustings of the pH to 5–6 values by addition of a 1:1 NH_4OH:C_2H_5OH solution were performed. The separated fine white crystalline products were filtered, washed with ethanol and dried.

The IR spectra (4000–400 cm^{-1}) were recorded with a BIORAD FTIR 1255 spectrophotometer. Thermal measurements were performed on a Q-1500 Paulik-Paulik-Erdey derivatograph, at heating rates of 5 K min^{-1} and with sample mass of ~40 mg. X-ray analysis was carried out by means of a Rigaku-Multiflex X-ray, with CuKα radiation.

Results and discussion

Characterization of the polynuclear coordination compounds

The elemental analysis is in good agreement with the following molecular formulae of the three coordination compounds used as precursor for magnesium-aluminium spinel:

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$$(NH_4)_4[Al_2Mg(C_4O_5H_4)_4(OH)_4]\cdot 2H_2O$$

$$(NH_4)_4[MgAl_2(C_4H_4O_6)_4(OH)_4]\cdot 3H_2O$$

$$(NH_4)_2[Al_2Mg(C_6O_7H_{11})_5(OH)_5]\cdot 3H_2O$$

where $C_4O_5H_4^{2-}$, $C_4H_4O_6^{2-}$ and $C_6O_7H_{11}^{2-}$ represent the dianions of malic, tartaric and gluconic acids.

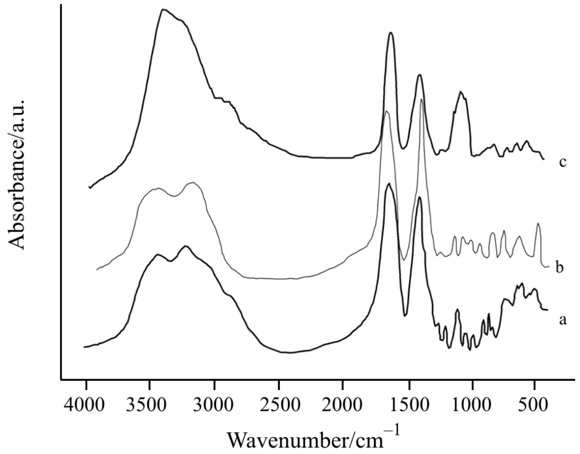

Fig. 1 IR spectra of the three polynuclear coordination compounds. a – $(NH_4)_4[Al_2Mg(C_4O_5H_4)_4(OH)_4]\cdot 2H_2O$; b – $(NH_4)_4[MgAl_2(C_4H_4O_6)_4(OH)_4]\cdot 3H_2O$; c – $(NH_4)_2[Al_2Mg(C_6O_7H_{11})_5(OH)_5]\cdot 3H_2O$

The polyhydrocarboxylic acids are bonded to the metallic ions through their COO^- and C–OH groups (Fig. 1(a–c)). The first affirmation is confirmed by the split of the free carboxylic group band (~1730 cm^{-1}) into two strong bands characteristic for coordinated carboxylic group, namely, $\nu_{OCOasym}$~1622/1668/1633 cm^{-1} and ν_{OCOsym}~1406/1391/1406 cm^{-1} (malate/tartrate/gluconate). A proof of the second affirmation, may the shift of the band assigned to $\nu_{(C–OH)}$ to lower frequencies (~1120→1100–980 cm^{-1}), which may arise also due to the formation of strong hydrogen bonds. The presence of the doublet at 1089 and 984 cm^{-1}/1089 and 1045 cm^{-1} in the case of tartrate/gluconate coordination compounds, means a dissimilarly coordination of the C–OH groups to two different metallic cations (Mg^{3+} and Fe^{3+}). Additional, all the compounds exhibit a strong and very wide band in the range 3600–3000 cm^{-1} assigned to the formation of hydrogen bonds between water and/or hydroxy groups. At the same time the presence on this wide band of two distinct peaks 3446, 3233 cm^{-1}/3440, 3165 cm^{-1}/3408, 3249 cm^{-1} (the last as shoulder, malate/tartrate/gluconate), sustain the existence of hydroxyl ($\nu_{OH\ free}$~3400 cm^{-1}) and NH_4^+ groups ($\nu_{NH_4^+}$~3195 cm^{-1}). The bands which appear in the 600–450 cm^{-1} range, in all the spectra, can be assigned to M–O stretching vibrations.

Thermal behaviour of the polynuclear coordination compounds

The three polynuclear coordination compounds underwent a 5/4/4 stepped decompositions in the temperature ranges 47–548.6°C/51–846°C/48–812°C (malate/tartrate/gluconate). The observed mass losses 80.84%/84.03%/88.24% are in good agreement with the calculated one considerring as end product magnesium-aluminum spinel (Fig. 2 (a–c)).

In the case of malate compound, $(NH_4)_4[Al_2Mg(C_4O_5H_4)_4(OH)_4]\cdot 2H_2O$, the decompo-

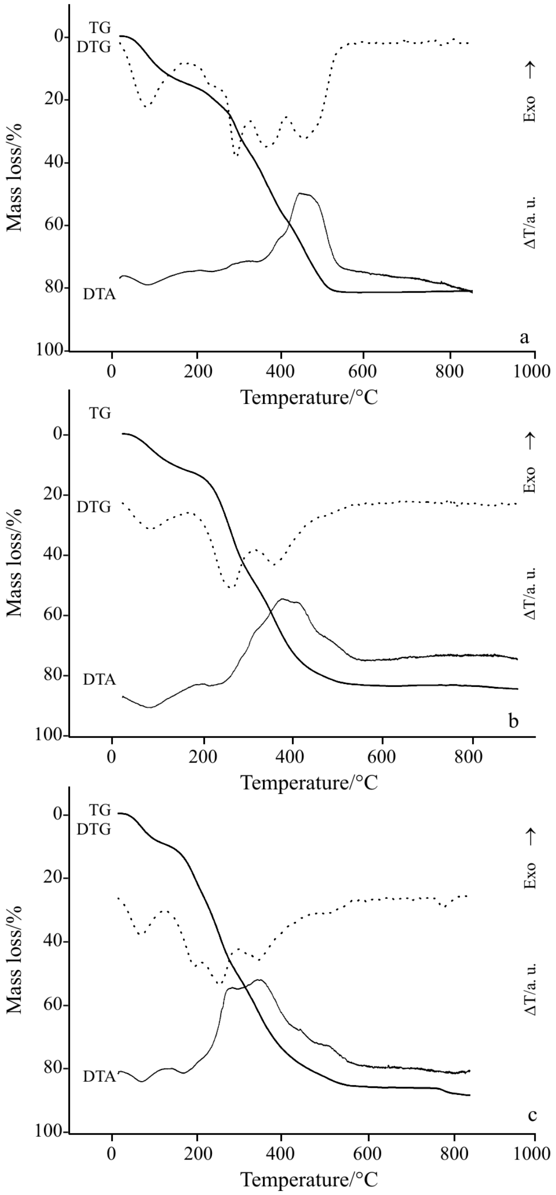

Fig. 2 TG, DTG and DTA curves for the three polynuclear compounds (heating rate=5°C min^{-1}, static air). a – $(NH_4)_4[Al_2Mg(C_4O_5H_4)_4(OH)_4]\cdot 2H_2O$; b – $(NH_4)_4[MgAl_2(C_4H_4O_6)_4(OH)_4]\cdot 3H_2O$; c – $(NH_4)_2[Al_2Mg(C_6O_7H_{11})_5(OH)_5]\cdot 3H_2O$

sition starts with two endothermic processes (47–182.5°C, $T_{\max\ DTG}$=81.2°C and 182.5–262.3°C, $T_{\max\ DTG}$=243°C), representing the evolving of four NH_3 and three H_2O molecules (calcd./found: 15.49/15.43%), respective three H_2O molecules (calcd./found: 6.78/7.15%). The disappearance of the peak from 3233 cm^{-1} after the first reaction step progress, validates this assumption. The next three decomposition steps (262.3–331.9°C, $T_{\max\ DTG}$=293.6°C; 331.9–406.5°C, $T_{\max\ DTG}$=363.9°C and 406.5–548.6°C, $T_{\max\ DTG}$=453.7°C) associated with exothermic effects, represent the degradative oxidation of the anionic ligand. The formation of magnesium-aluminum spinel via malonate and oxoacetate intermediates, is confirmed both by stoichiometric calculations (malonate intermediate: calcd./found: 15.95/15.60%, oxoacetate intermediate: calcd./found: 17.89/18.78%, spinel end product: calcd./found: 25.89/23.88%) and IR investigations. The formation of malonate intermediate is evidenced in IR spectra by a gradual decrease till disappearance of the band characteristic to C–OH group (~1080 cm^{-1}) and a shift towards lower frequencies of the $\nu_{OCOasym}$ (1622→1599 cm^{-1}). A shoulder at ~1300 cm^{-1} and a weak band at ~1050 cm^{-1} characteristic for CH_3^- group of acetate, are identified at the intermediate isolated at 400°C. The formation during the thermal decomposition of malate compounds of malonic [31–36] and oxoacetate [32–38] intermediates is already reported by literature.

The second coordination compound, the tartrate compound $(NH_4)_4[MgAl_2(C_4H_4O_6)_4(OH)_4]\cdot 3H_2O$, suffers a first endothermic decomposition process (51–168°C, $T_{\max\ DTG}$=80°C) corresponding to the evolving of four NH_3 and three H_2O molecules (calcd./found: 12.03/12.38%). The second decomposition process (168–316°C, $T_{\max\ DTG}$=262.6°C), associated initial with an endothermic effect which is further converted into an exo one, corresponds to the elimination of remaining three water molecules and the outset degradation of the tartaric anion ligand with formation of an oxalate intermediate (calcd./found: 38.18/37.23%). The IR spectra of the intermediate isolated at 300°C presents only three strong bands: two corrresponding to $\nu_{OCOasym}$ and ν_{OCOsym} shifted to lower (1668→1620 cm^{-1}) and respective higher wavenumbers (1391→1446 cm^{-1}) and a third wide one in the range 440–800 cm^{-1} with an individual maxima at 690 cm^{-1}, corresponding to M–O stretching vibrations. At further heating (316–562°C, $T_{\max\ DTG}$=354.7°C), a complex exothermic process occurs, the DTG curve registering two maxima and a shoulder (378, 409 and ~492°C). This step is consistent with the decomposition of oxalate intermediate via a hydroxycarbonate of hydrotalcite type ($Mg_6Al_2(OH)_{16}CO_3\cdot H_2O$) to an oxocarbonate with molecular formula $Al_2MgO_{3.66}(CO_3)_{0.33}$ (calcd./found: 31.36/32.43%). During this temperature interval, the bands corresponding to $\nu_{OCOasym}$ and ν_{OCOsym} loss symmetries and shift to lower respective higher wavenumber, overlapping. The entire combinations is similar with the principal band of carbonate at 1390 cm^{-1}. Other two weak bands characteristic to carbonate at 873 and 665 cm^{-1} are identified. The formation of an intermediate of hydrotalcite type ($Mg_6Al_2(OH)_{16}CO_3\cdot H_2O$) is sustained by the presence in the IR spectra of the intermediates isolated at 400 and 500°C of the bands characteristic to the presence of HO^- group (weak band at ~3730 cm^{-1} and a shoulder at ~1700 cm^{-1}) and water (a relative wide band in 3600–3000 cm^{-1} range with a maximum at 3300 cm^{-1}). The last decomposition step (562–846°C), represents a gradual continuous evolving of CO_2 and Al_2MgO_4 formation (calcd./found: 1.69/1.49%).

The thermal decomposition of the gluconate coordination compound, $(NH_4)_2[Al_2Mg(C_6O_7H_{11})_5(OH)_5]\cdot 3H_2O$, starts with two endothermic processes (48–131°C, $T_{\max\ DTG}$=70.6°C and 131–205.3°C, $T_{\max\ DTG}$=193°C). The first one corresponds to the evolving of two ammonia and five water molecules (calcd./found: 10.09/9.77%). The stoichiometric calculation for the second endothermic decomposition step leads to the assumption that eight water molecules are eliminated, (calcd./found: 11.72/12.25%), three from coordination sphere and five due to an internal condensation of the gluconate anion ligand [39]. A further increasing of the temperature, determines an oxidative fragmentation of the anionic gluconic ligand (205.3–601.3°C). The degradation process is complex, three maximum being detected on DTG curve (254.9, 341.9 and 503.3°C) and four on DTA one (271.7, 344.7, 493.5 and 511.2°C). Due to the complexity of the process, it was not possible to identify the corresponding reaction intermediates. At 601.3°C, the formation of an oxocarbonate with molecular formula $Al_2MgO_{3.66}(CO_3)_{0.33}$ (calcd./found: 64.25/63.71%), characterized by vibration bands at ~1400, 880 and 670 cm^{-1} is proposed, which decomposes in a well defined step (741.2–812.0°C) to Al_2MgO_4 (calcd./found: 2.36/2.45%).

Final oxides characterization

The formation of magnesium-aluminum spinel ($MgAl_2O_4$) as final decomposition oxides is confirmed for the oxides derived from all three polynuclear coordination compounds. Figure 3 presents the X-ray diffractogram of the spinel oxide ob-

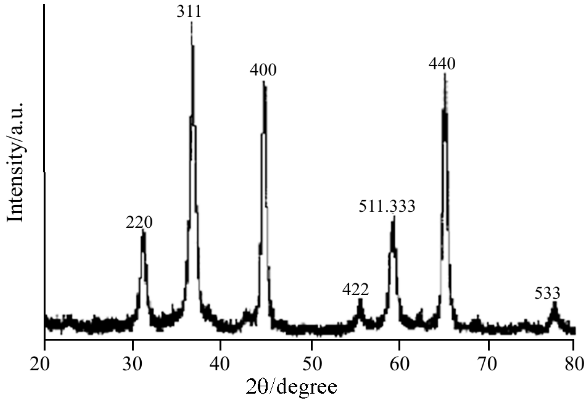

Fig. 3 X-ray diffractogram of Al_2MgO_4 obtained from gluconic coordination compound precursor (1000°C–1 h)

tained from gluconic precursor. The nature of the ligand, influence the final decomposition temperature, and implicit the values of the mean crystallite size. If, for malate derived oxide, it was possible to achieve the spinel lattice after a calcination time of one hour at 800°C, the spinel oxides obtained from tartrate and gluconate coordination compounds, need a thermal treatment of 1 h at 1000°C. As a consequence, the mean particle size values varies in the following order: malate<gluconate<tartrate: 143 Å<165 Å<180 Å. The lower values obtained for the $MgAl_2O_4$ synthesized from gluconate compound comparative with tartrate, although they were subjected to same heating treatment, may be connected with the higher amount of evolved gases (due to higher content and size of gluconate anion ligand).

Conclusions

The following decomposition schemes are proposed for the three polynuclear coordinations compounds:

malate compound:

$$\mathrm{(NH_4)_4[Al_2Mg(C_4H_4O_5)_4(OH)_4]\cdot 2H_2O} \xrightarrow{47-182.5^\circ C}$$

$$\mathrm{[Al_2Mg(C_4H_4O_5)_4(H_2O)_3]} \xrightarrow{182.5-262.3^\circ C}$$

$$\mathrm{[Al_2Mg(C_4H_4O_5)_4]} \xrightarrow{262.3-332^\circ C}$$

$$\mathrm{[Al_2Mg(C_3H_2O_4)_4]} \xrightarrow{332-406.5^\circ C}$$

$$\mathrm{[Al_2Mg(C_2H_3O_3)_4O_2]} \xrightarrow{406.5-548.6^\circ C} \mathrm{Al_2MgO_4}$$

tartrate compound:

$$\mathrm{(NH_4)_4[Al_2Mg(C_4H_4O_7)_4(OH)_4]\cdot 3H_2O} \xrightarrow{51-168.6^\circ C}$$

$$\mathrm{[Al_2Mg(C_4H_4O_7)_4(H_2O)_5]} \xrightarrow{168.6-316^\circ C}$$

$$\mathrm{[Al_2Mg(C_2O_4)_4]} \xrightarrow{316-562^\circ C}$$

$$\underset{\text{intermediate}}{\mathrm{[Mg_6Al_2(OH)_{16}CO_3\cdot H_2O]}} \longrightarrow$$

$$\mathrm{Al_2MgO_{3.66}(CO_3)_{0.33}} \xrightarrow{562-846^\circ C} \mathrm{Al_2MgO_4}$$

gluconate compound:

$$\mathrm{(NH_4)_2[Al_2Mg(C_6H_{11}O_7)_5(OH)_5]\cdot 3H_2O} \xrightarrow{48-131.1^\circ C}$$

$$\mathrm{[Al_2Mg(C_6H_{11}O_7)_5(OH)_3]} \xrightarrow{1.\ 131.1-205.3^\circ C}$$

$$\xrightarrow[2.\ 205.3-299^\circ C/\ 3.\ 299-601.3^\circ C]{} \mathrm{Al_2MgO_{3.66}(CO_3)_{0.33}}$$

$$\xrightarrow{741-812^\circ C} \mathrm{Al_2MgO_4}$$

The thermal decomposition of malate coordination compounds is ended at lower temperature (549°C) comparative with tartrate and gluconate ones (846 and 812°C), above all due to the absence of oxocarbonate intermediate. As an effect, for magnesium-aluminum spinel synthesis, heating treatments of one hour at 1000°C are needed for gluconate and tartrate derived oxides comparative with 1 h at 800°C for malate derived one. The mean particle size values of the obtained spinels vary in the following order: malate<gluconate<tartrate: 143 Å<165 Å< 180 Å. The lower values find for the $MgAl_2O_4$ synthesized from gluconate compound comparative with tartrate, although they were subjected to same heating treatment, may be connected with the higher amount of evolved gases during precursor decomposition, which hinder the sintering.

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