

Mg-Al AND Mg-In OXIDE COMPOUNDS AS CATALYST COMPONENTS FOR THE OXIDATIVE DEHYDROGENATION OF PROPANE. PART II

CHARACTERIZATION OF THE CALCINED MATERIALS

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Received November 20, 2006

Various oxide phases have been obtained by thermal decomposition of Mg-Al and Mg-In materials. The effect of the preparation mode (either co-precipitation or evaporation) of the precursors and the nature of the trivalent cation on the thermal stability and structure of the generated oxide phases was investigated by thermogravimetric and thermal analysis, BET surface area measurements, X-rays diffraction and IR spectroscopy. The evaporated samples decomposed to oxide materials at lower temperature than the co-precipitated ones. The co-precipitated Mg-Al compound showed higher thermal stability than the co-precipitated Mg-In one. The phase of MgO was registered in all calcined samples while Al₂O₃ phase was X-ray amorphous independently of the synthesis procedure. On contrary, In₂O₃ was well crystallized in two polymorphous forms, cubic and rhombohedral in the calcined co-precipitated sample and only in the cubic one in the calcined evaporated one. The mean particle size of MgO phase in co-precipitated MgAl-LDH material was about 2 times smaller than in MgIn-LDH one, correlating with the increase of the specific surface area. Both effects demonstrated the dispersion role of the Al³⁺ in the Mg-Al co-precipitated oxide material. This phenomenon was not observed in both evaporated oxides. The property of Al³⁺ to form spinelic phases with Mg²⁺ was demonstrated in both co-precipitated and evaporated Mg-Al samples by appearance of short range ordered prespinelic structures.

INTRODUCTION

This paper represents the Part II of the study about the preparation and characterization of Mg-Al and Mg-In oxide systems as catalyst components for the oxidative dehydrogenation of propane.¹ Part I was dealing with the investigation of the effects of the preparation method (co-precipitation or evaporation) and on the presence of trivalent cation (Al³⁺ or In³⁺) on the structure of Mg-Al and Mg-In layered double hydroxides or nitrates. It was established that the co-precipitation procedure provoked the formation of hydrotalcite-like structure containing NO₃⁻ anions in the interlayer space. The presence of Al³⁺ ions caused the formation of a LDH single-phase material of smaller particle size and higher surface area in comparison to that of In³⁺. The latter cation

induced the additional appearance of In(OH)₃ phase with large particle size. The evaporation procedure led to formation of a mixture of magnesium and aluminium nitrate hydrate phases for Mg-Al compound, and a mixture of magnesium nitrate hydrate and cubic indium oxide for Mg-In compound. Part II continues the investigation of the same effects on the structure of the Mg-Al and Mg-In oxide materials formed after thermal treatment of the starting materials. The oxide Mg-Al and Mg-In systems represent components of the Mg-Al-V and Mg-In-V catalysts for propane ODH reaction. The Mg presence is bringing the basic character, Al and In are tuning it, thus selectivity to propene, and V is bringing more activity.

The main aim in mixed oxides preparation is to attain a high dispersion of the cations, avoiding segregation of the different phases, which can

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possibly be formed.² One of the methods, currently applied to achieve a high dispersion, is the synthesis layered double hydroxides (LDHs) as precursors and to calcine them carefully. The thermal treatment of LDHs includes dehydration, dehydroxylation and loss of the charge compensating anions, resulting in mixed oxides of $M^{2+}(M^{3+})O$ type. These mixed metal oxides represent promising catalyst precursors or supports due to their large surface area, high metal ion dispersion, and stability against sintering and basic properties. The basicity of the obtained materials depends on various parameters such as nature and ratio of the cations M^{2+} and M^{3+} as well as the applied thermal treatment.²⁻⁴ The different basic character of the cations is expected to affect their activity and selectivity.

EXPERIMENTAL PART

Sample preparation

Mg-Al and Mg-In oxidic compounds with chemical composition $Mg^{2+}/M^{3+} = 3/1$ ($M^{3+} = Al^{3+}$ or In^{3+}) have been prepared either by co-precipitation or by evaporation methods. Detailed description of the preparation procedures is reported in Part I.¹ The samples were thermally treated at 550°C for 3 h in order to obtain mixed metal oxides with theoretical composition of 86 mol % MgO and 14% mol % Al_2O_3 (In_2O_3) or 70 wt % MgO - 30 wt % Al_2O_3 and 47 wt % MgO - 53 wt % In_2O_3 , respectively. The co-precipitated samples were denoted as MgAl-LDH and MgIn-LDH and the evaporated ones as MgAl and MgIn, respectively.

Sample characterization

The thermal analysis (DTG-TG) of the synthesized materials was carried out with a SETARAM TGDTA92 thermobalance in air at a heating rate of 2.5°C min⁻¹.

The composition of the final oxide materials was determined by ICP-AES and their specific surface area measured employing the single point analysis method using a Micromeritics Instrument, FlowSorb 2300, based on the N₂/He (30/70) adsorption at liquid nitrogen temperature.

The metal oxides were characterised by X-ray diffraction (XRD) analysis. The XRD measurements were carried out with TUR-M 62 powder diffractometer employing $CuK\alpha_1$ radiation ($\lambda = 0.1540$ nm) at 40 kV and 30 mA with a scanning speed 2θ of 2° min⁻¹. The crystalline phases were identified using the Joint Committee on Powder Diffraction Standards (JCPDS) files. The lattice parameter (a) and the total cell volumes (V_t) of the oxides were determined using Unit Cell computer program.⁵ The mean particle size (L) was determined from the line broadening reflections, using the Scherer equation. The calculations were done using FIT computer program.⁶

The infrared (IR) spectra of the calcined samples were recorded with a Specord M 80 type Carl Zeiss Jena spectrometer. The spectra were registered using the KBr pellet technique: 0.5 mg of each sample was mixed with 200 mg of KBr (KBr for spectroscopy Uvasol, Merck), in the spectral range 1800- 400 cm⁻¹ with a resolution of 4 cm⁻¹.

RESULTS AND DISCUSSION

The thermal decomposition of the as-prepared nitrate-containing LDHs samples was monitored by TG-DTA analysis. The main steps in the weight loss of the samples are listed in the Table 1.

Table 1

Summary of the TG-DTA results

Sample	I step		II step		III step		Total weight loss (%)
	t (°C) range	wt. loss (%)	t (°C) range	wt. loss (%)	t (°C) range	wt. loss (%)	
MgAl-LDH	70–200	10.2	360–430	18.5	430–490	6.5	42.5
MgIn-LDH	70–180	7	300–370	14.5	370–470	10	33.0
MgAl	100–190	9	-	-	390–450	45	69.3
MgIn	-	-	-	-	390–470	47	57.8

The co-precipitated samples, MgAl-LDH and MgIn-LDH, showed three main weight loss steps. The decomposition of MgIn-LDH sample proceeded at lower temperatures and total weight losses were less than for MgAl-LDH sample (Table 1). The process was almost completed in the range of 500–600°C, weight losses being of 2.2 and 2.4 wt %, respectively (Figs. 1 and 2). The DTA curves of both co-precipitated samples exhibited two well-pronounced endothermic peaks at 130 and 390-415°C (MgAl-LDH) or 350°C (MgIn-LDH). A weak endothermic shoulder at

about 465°C was observed for MgAl-LDH sample (Fig. 1) and a distinct one - at about 430°C for MgIn-LDH sample (Fig. 2). The first peak was attributed to the loss of interlayer water molecules. The second ones reflect the elimination of the nitrate ions from the interlayer and the dehydroxylation of the brucite-like layers. The increasing trend of the DTA curves was more pronounced for MgAl-LDH sample and the high temperature shoulders indicated that the decomposition process and/or phase transformations were not finished yet.

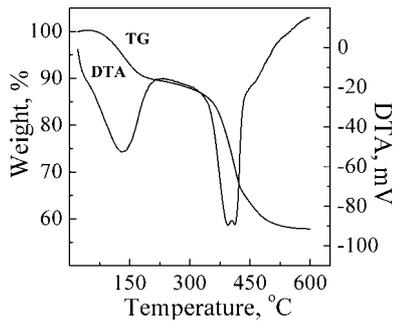


Fig. 1 – TG-DTA curves of MgAl-LDH.

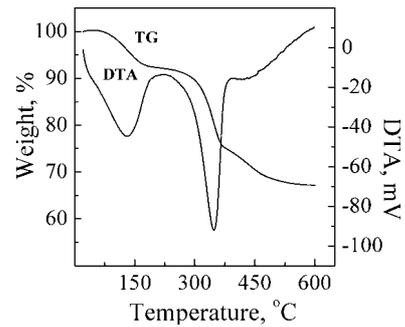


Fig. 2 – TG-DTA curves of MgIn-LDH.

It must be noted that the second endothermic peak and the high temperature shoulder in In-containing material were shifted to lower

temperature. Both TG-DTA analyses revealed the lower thermal stability of the co-precipitated Mg-In compound.

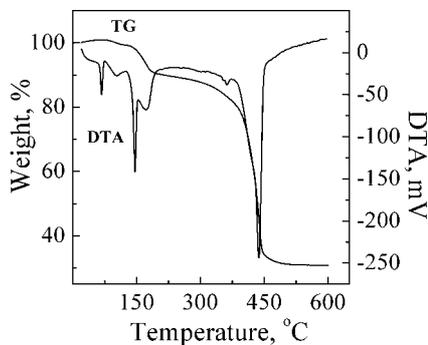


Fig. 3. TG-DTA curves of MgAl.

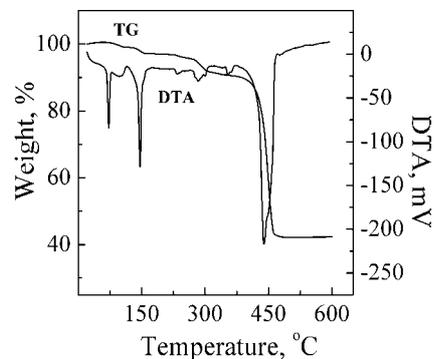


Fig. 4. TG-DTA curves of MgIn.

The TG curve of the evaporated MgAl sample showed two main weight loss steps, while the MgIn showed only one (Fig. 3 and 4). The decomposition of both samples proceeded in the same temperature range (Table 1) and were complete at 450–600°C (MgAl) and 490–600°C (MgIn), respectively; the weight losses being less than 1 wt % (Fig. 3 and 4). The DTA curves of the evaporated samples MgAl and MgIn (Figs. 3 and 4) exhibited

similar thermal behaviour. Various endothermic peaks were located in the low temperature range 60–200°C, related to the dehydration processes. The main endothermic peaks at 440°C may be ascribed to NO_3^- ions decomposition evolving NO_x . The slight trend of the curves after 450°C proves the completion of the solid phase process.

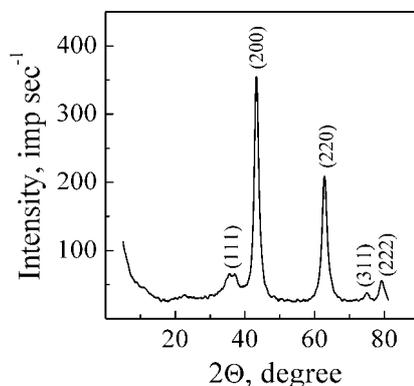


Fig. 5 – XRD pattern of MgAl-LDH.

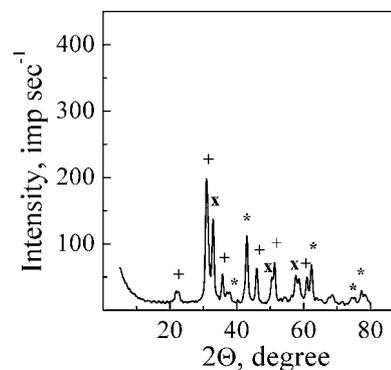


Fig. 6 – XRD pattern of MgIn-LDH:
 (*) - MgO, (+) - cubic In_2O_3 and (x) - rhombohedral In_2O_3 .

The XRD patterns of MgAl-LDH (Fig. 5) displayed peaks at $d = 0.2427, 0.2091, 0.1480, 0.1268$ and 0.1217 nm, corresponding to (111), (200), (220) (311) and (222) reflections typical of single crystalline phase MgO, periclase (JCPDS file 45-0946). No reflections of Al_2O_3 phase

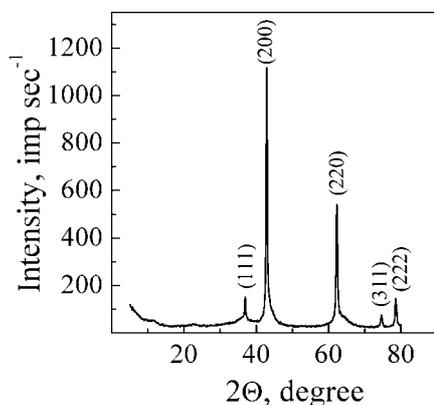


Fig. 7 – XRD patterns for oxide MgAl.

The additional peaks observed at $d = 0.4099, 0.2890, 0.2511, 0.2378, 0.1976, 0.1780,$ and 0.1519 nm can be related to the (211), (222), (400), (411), (431), (440) and (622) reflections characteristic of cubic In_2O_3 (JSPDS file 06-0416) and the peaks at $d = 0.2720, 0.1806, 0.1598$ and 0.1574 nm - to the (110), (116), (214) and (300) reflections typical of rhombohedral In_2O_3 (JSPDS file 22-0226).

Similar results were obtained during the decomposition of the evaporated materials. Both MgAl (Fig. 7) and MgIn sample (Fig. 8) showed reflections of MgO phase, better crystallized than the co-precipitated ones. No reflections of Al_2O_3 phase appeared, too. In addition, reflections characteristic only of cubic In_2O_3 were registered for MgIn sample on contrary to the co-precipitated Mg-In-LDH sample. The lattice parameter, a_{MgO} ,

appeared. The patterns of MgIn-LDH were more complex (Fig. 6). The reflections of MgO phase also appeared, but with diffraction lines located at values d higher the values of d for Mg-Al, namely $0.2430, 0.2102, 0.1487, 0.1275$ and 0.1221 nm.

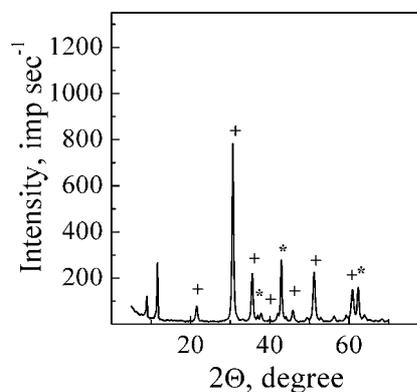


Fig. 8 – XRD patterns for oxide MgIn: (*) MgO and (+) cubic In_2O_3 .

was calculated from the most intense MgO reflection (200) (Table 2). It can be remarked that the value of parameter a in both co-precipitated oxides was lower than in the pure standard MgO (JCPDS file 45-0946). The differences may be ascribed to the presence of Al^{3+} or In^{3+} cations in the MgO lattice⁷ due to the mixed oxides formation. The effect of In^{3+} ions was less pronounced because of its higher ionic radii (0.081 nm) than Al^{3+} (0.053 nm). The presence of In_2O_3 phase in the calcined product was due to the formation of single phase of $In(OH)_3$ in the as-synthesized material (see Part I). The values of the lattice parameter and lattice volume of both evaporated oxides were equal and very close to the standard MgO sample. This indicated predominant formation of MgO in MgAl sample and a mixture of oxides in MgIn sample.

Table 2

Specific surface area (SSA) and structural characteristics of the calcined materials

Sample	SSA ($m^2 g^{-1}$)	Structural characteristics of MgO phase		
		a (nm)	V (nm^3)	$L_{(200)}$ (nm)
MgAl-LDH	195	0.4182 ± 0.0002	0.073 ± 0.001	7
MgIn-LDH	93	0.4204 ± 0.0001	0.074 ± 0.001	13
MgAl	62	0.4212 ± 0.0001	0.075 ± 0.001	22
MgIn	51	0.4212 ± 0.0001	0.075 ± 0.001	24
MgO*	-	0.4211	0.075 ± 0.001	-

*(MgO, JCPDS file 45-0946)

The particle size (L) of the oxide materials was estimated from the values of the full-width at half-maximum of the MgO (200) diffraction peaks. The mean particle size of co-precipitated oxide MgAl-LDH was about 2 times smaller than the MgIn-LDH one (Table 2), in agreement with the increase of the specific surface area. Both effects demonstrated the dispersion role of the Al^{3+} in the Mg-Al co-precipitated oxide materials. Both evaporated oxides exhibited close values of the mean particle size and specific surface area, respectively. XRD data showed that the thermal activation at 550°C of both co-precipitated samples destroyed their layered structure. Its collapse led to mixed metal oxides ($\text{MgO-M}_2\text{O}_3$) in MgAl(In)-LDH with more developed surface area than the mixture of oxides obtained by calcination of the evaporated materials. Independently of the synthesis procedures Al_2O_3 phase was X-ray amorphous. On contrary, In_2O_3 was well crystallized, existing in two polymorphous forms, cubic and rhombohedral in the calcined co-precipitated sample and only in the cubic one in the calcined evaporated one.

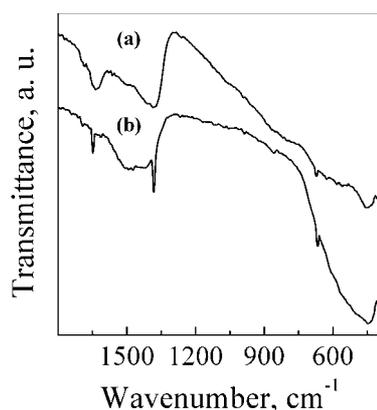


Fig. 9 – IR spectrum for oxides: (a) MgAl-LDH and (b) MgIn-LDH.

The IR spectrum of MgAl sample obtained by calcinations of the evaporated material (Fig. 10, **a**) showed absorption bands similar to the MgAl-LDH one (Fig. 9, **a**) related to the water molecule bending vibration (1650 cm^{-1}), CO_3 ions (1375 cm^{-1}) and more pronounced evidence for short range ordered Mg-Al pre-spinelic structure (shoulder at 800 cm^{-1}). Only absorption band in the low-frequency $800\text{--}400\text{ cm}^{-1}$ region, typical to the M–O lattice vibrations was registered for MgIn material (Fig. 10, **b**). This confirmed the complete sample decomposition, illustrated by the thermal analysis data (Fig. 4).

The infrared spectra of MgAl-LDH sample obtained by calcination of the co-precipitated material (Fig. 9, **a**) showed absorption band around 1650 cm^{-1} corresponding to water molecule bending vibration, $\delta\text{H}_2\text{O}$, ν_3 mode at 1375 cm^{-1} , characteristic for CO_3 ions and a very broad asymmetric band in the low-frequency $800\text{--}400\text{ cm}^{-1}$ region, typical of the M–O lattice vibrations. The shoulder at 740 cm^{-1} may be related to the appearance of isolated AlO_4 tetrahedra characteristic to the Mg-Al pre-spinelic structure.⁸ There was no evidence of NO_3 ions existence. On contrary, the narrow bands of ν_3 mode at 1380 and ν_4 mode at 670 cm^{-1} , typical of NO_3 ions, registered in co-precipitated MgIn-LDH material¹ were still observed in the calcined sample MgIn-LDH (Fig. 9, **b**). Obviously, part of NO_3 ions remained un-decomposed in the oxide material. The absorption band in the low-frequency $800\text{--}400\text{ cm}^{-1}$ region more intensive and symmetric, indicating more uniform M–O lattice vibrations.

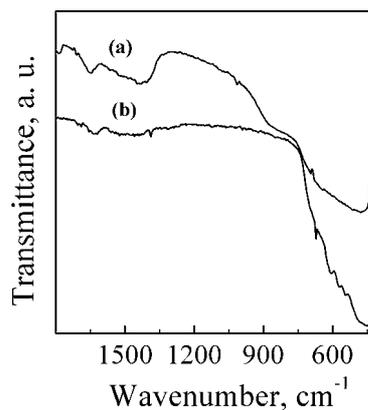


Fig. 10 – IR spectrum for oxides: (a) MgAl and (b) MgIn.

CONCLUSIONS

The preparation procedure and the nature of the trivalent cation have been shown to influence the thermal stability of the precursors and the structure of the oxide materials. The evaporated materials fully decomposed at lower temperature than the co-precipitated ones. The co-precipitated Mg-Al compound showed higher thermal stability than the co-precipitated Mg-In one. Only the calcined co-precipitated MgIn sample contained small quantity of un-decomposed starting material. The thermal treatment of both co-precipitated samples collapsed their layered structure. Mixed metal

oxides were formed with more developed surface area comparative to the mixture of oxides in the evaporated materials. The phase of MgO was registered in all calcined samples, while the nature of the M^{3+} ion reflected on the degree of oxide crystallinity. It was noted that Al_2O_3 phase was X-ray amorphous, independently of the synthesis procedure, whereas In_2O_3 was well crystallized in two polymorphous forms, cubic and rhombohedral in the calcined co-precipitated sample and only in the cubic one in the calcined evaporated one. The property of Al^{3+} to form spinelic phases with Mg^{2+} was demonstrated in both co-precipitated and evaporated Mg-Al samples by appearance of short range ordered prespinelic structures.

The mean particle size of MgO phase in co-precipitated MgAl-LDH material was about 2 times smaller than the MgIn-LDH one, correlating with the increase of the specific surface area. Both effects demonstrated the dispersive role of the Al^{3+} in the Mg-Al co-precipitated oxide material. On the contrary, this phenomenon was not observed in

both evaporated oxides, possessing close values of the mean particle size and specific surface area.

ACKNOWLEDGEMENTS: The financial support by the French Ministry of National Education and Research, through RILA project and the National Science Funds in Bulgaria (program "Rila") and Romania (program "Brâncuși") is gratefully acknowledged.

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