

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

PREPARATION AND CHARACTERIZATION OF THE AS-SYNTHEZIZED MATERIALS

Margarita GABROVSKA,^{a*} Rumeana EDREVA-KARDJIEVA,^a Verislav ANGELOV,^a Dorel CRIȘAN,^b Gabriel MUNTEANU^b and Jacques VÉDRINE^c

^a Institute of Catalysis, Bulgarian Academy of Sciences, Acad. G. Bonchev bl. 11, 1113 Sofia, Bulgaria

^b Institute of Physical Chemistry, Roumanian Academy, Independenței 202, 060021 Bucharest-12, Roumania

^c Laboratoire de Réactivité de Surface, Tour 54-55, Université P. & M. Curie, 4, place Jussieu, F-75252, Paris, France

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Mg-Al and Mg-In compounds with the chemical composition of $Mg^{2+}/M^{3+} = 3/1$ have been prepared either by co-precipitation or by evaporation methods using nitrate salts as starting materials. The effect of the preparation method on the structure of the solids has been investigated by BET-surface area measurements, X-rays diffraction (XRD) and Infrared spectroscopy (IR). XRD data showed that the co-precipitation procedure led to layered double hydroxides with hydrotalcite-like-structure. The presence of Al^{3+} ion determined the formation of a well crystallized single-phase of smaller particle size (5 nm) and higher surface area ($130 \text{ m}^2 \text{ g}^{-1}$) as compared with In^{3+} ion (13 nm and $80 \text{ m}^2 \text{ g}^{-1}$, respectively). In the latter case indium hydroxide of 17 nm particle size was formed. The IR study confirmed that the nitrate ions in the interlayer are not exchanged by carbonate ones during the preparation procedure. The evaporation procedure led to the appearance of magnesium and aluminium nitrate hydrate phases in Mg-Al compound, while magnesium nitrate hydrate and cubic indium oxide were observed for the Mg-In sample.

INTRODUCTION

Oxidative dehydrogenation (ODH) of light alkanes into their corresponding alkenes represents a challenge in the contemporary science and industry due to the increased demand of alkenes. ODH of light alkanes (C_2 to C_4) is an attractive route to convert low cost saturated hydrocarbons into more valuable unsaturated hydrocarbons. Alkenes, especially ethene and propene, are used as feedstock for the polymer industry.¹ It has been found that Mg-V-O mixed oxide system is one of the most active and selective in the ODH of propane to propene,²⁻⁴ but their catalytic properties are strongly influenced by the preparation procedure.⁵ These catalysts are usually prepared either by impregnation of MgO or $Mg(OH)_2$ with a suitable solution of a soluble vanadium salt, followed by high-temperature calcination, or by solid state reaction between Mg and V oxides. It may be generalized that the activity and selectivity

of Mg-V catalysts depend on the V/Mg ratio and on the kind of the formed oxide phases. The ability of the catalyst to yield propene or CO_x has been shown to be related to the acidic-basic sites on its surface for instance basic sites has been observed to favour fast desorption of olefin intermediates, finally yielding alkenes,⁶ while V cation, a Lewis acid site, is known to activate alkanes. It has been reported that Mg-V-Al mixed oxides, obtained by thermal decomposition of Mg-Al layered double hydroxides containing vanadium either in the brucite layer, or in the interlayer, could be promising catalysts for ODH of propane.⁷

Layered double hydroxides (LDHs) belong to a class of anionic clays with hydrotalcite-like structure. These compounds possess positively charged brucite-like hydroxide layers $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}$, which are neutralized by interlayer anions $[A^{n-}]_{x/n} \cdot mH_2O$ and water molecules.⁸ A wide variety of divalent ($M^{2+} = Mg^{2+}, Ni^{2+}, Co^{2+}$, etc.) or trivalent ($M^{3+} = Al^{3+}, Cr^{3+}, Fe^{3+}$, etc.) cations having an ionic

* Corresponding author: margo@ic.bas.bg

radius similar to that of Mg^{2+} may be accommodated in an appropriate ratio ($1.5 < M^{2+}/M^{3+} < 4$) in the octahedral sites in the brucite-type sheets thus changing the structure and properties of the LDHs formed. It has been reported that the layered compounds can host different exchangeable anions in the interlayer space ($A = CO_3^{2-}, NO_3^-, OH^-,$ etc.). An important feature of LDH is the relative facility of anion exchange.^{9,10} Further direct changes of the structure and properties of the LDHs may occur.

The purpose of this work was to investigate the effects of the preparation method (co-precipitation or evaporation) and of the presence of trivalent cations (Al or In) on the structure of Mg-Al and Mg-In materials as basic components of ODH catalysts.

EXPERIMENTAL PART

Sample preparation

All the chemicals used in the sample synthesis are of "pro analysis" purity grade.

Co-precipitation procedure

The LDHs were obtained by co-precipitation of the mixed metal nitrate solution containing the Mg^{2+} and M^{3+} ($M^{3+} = Al^{3+}$ or In^{3+}) ions in the ratio of $Mg^{2+}/M^{3+} = 3.0/1$ with 2M NaOH solution. The synthesis was carried out under Ar atmosphere to avoid the presence of CO_3^{2-} ions in the precipitates. The preparation procedure was performed at room temperature, constant value of $pH = 10 \pm 0.1$ and under vigorous stirring. The slurry was aged in mother liquor at $55^\circ C$ for 4 h under the same conditions. The precipitates were filtered and washed with small quantity of deionized water to keep the NO_3^- ions in the interlayer space of the materials. The precipitates were then dried in an oven at $65^\circ C$ for 20 h. These co-precipitated samples were denoted as MgAl- NO_3 -LDH and MgIn- NO_3 -LDH, respectively.

Evaporation procedure

Two mixed nitrate solutions containing Mg^{2+} and M^{3+} ($M^{3+} = Al^{3+}$ or In^{3+}) ions in the ratio of $Mg^{2+}/M^{3+} = 3.0/1$ were prepared. The first one consisted of 0.18 mol $Mg(NO_3)_2 \cdot 6H_2O$ and 0.06 mol $Al(NO_3)_3 \cdot 9H_2O$, respectively. The second one contained 0.12 mol $Mg(NO_3)_2 \cdot 6H_2O$ and 0.04 mol $In(NO_3)_3 \cdot H_2O$, respectively. The corresponding solutions were heated under vigorous stirring for 2 h up to obtaining a highly consistent solution. The evaporation procedure was continuing on a sand bath at $200^\circ C$ up to the formation of a solid compound. The evaporated samples were denoted as MgAl- NO_3 and MgIn- NO_3 , respectively.

Sample characterization

The samples were dried at $80^\circ C$ for 20 h before characterization. The composition of the materials was determined by ICP-AES. The specific surface area of the materials was measured employing the single point surface analysis (Micromeritics Instrument, FlowSorb 2300), based on the N_2/He (30/70) adsorption.

The samples were characterised by X-ray diffraction (XRD) analysis. The measurements were carried out with a conventional powder diffractometer employing $CuK\alpha_1$ radiation ($\lambda = 0.1540$ nm) at 40 kV and 30 mA on 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 parameters (a and c) and the total cell volumes (V_t) of the samples were determined using Unit Cell computer program.¹¹ The mean particle size (L) was determined from the line broadening reflections, using the Scherer equation. The calculations were done using FIT computer program.¹² Infrared spectra (IR) were recorded with a Specord M 80 type Carl Zeiss Jena spectrometer in the range from 1800 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1} using the KBr pellet technique: 0.5 mg of each sample was mixed with 200 mg of KBr (KBr for spectroscopy Uvasol, Merck).

RESULTS AND DISCUSSION

The chemical composition of the Mg-Al and Mg-In materials in the starting solutions and in the obtained solid samples is presented in Table 1.

Table 1

Chemical composition of the starting solution and of the prepared materials

Notation	Chemical composition	
	Mg^{2+}/M^{3+} ratio (theoretical)	Mg^{2+}/M^{3+} ratio (experimental)
MgAl- NO_3 -LDH	$Mg^{2+}/Al^{3+} = 3.0/1$	$Mg^{2+}/Al^{3+} = 2.85/1$
MgIn- NO_3 -LDH	$Mg^{2+}/In^{3+} = 3.0/1$	$Mg^{2+}/In^{3+} = 2.84/1$
MgAl- NO_3	$Mg^{2+}/Al^{3+} = 3.0/1$	$Mg^{2+}/Al^{3+} = 2.99/1$
MgIn- NO_3	$Mg^{2+}/In^{3+} = 3.0/1$	$Mg^{2+}/In^{3+} = 2.98/1$

The Mg^{2+}/M^{3+} ratios in the as-prepared samples are nearly equal to the corresponding ratios in the synthesis solutions. The results demonstrated that the Mg^{2+} , Al^{3+} and In^{3+} ions are quantitatively precipitated and evaporated.

The XRD pattern for the co-precipitated sample MgAl- NO_3 -LDH (Fig. 1) displayed well-defined

peaks at $d = 0.8022, 0.3990, 0.2589, 0.2341, 0.1990, 0.1526$ and 0.1517 nm, which can be related to the (003), (006), (009), (015), (018), (110) and (113) reflections of hydrotalcite (JCPDS file 14-0191). The reflections with indexes (009), (015) and (018) showed a strong asymmetry, with a tail towards the larger angles. This pointed out

that the sample MgAl-NO₃-LDH consisted of very small crystallites (Table 2). No additional phases

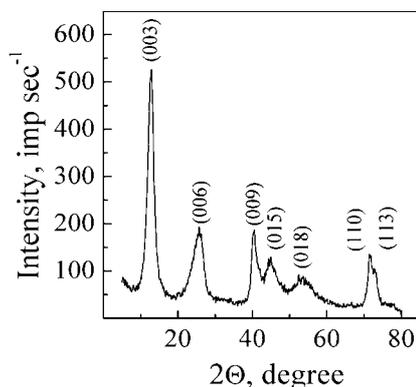


Fig. 1 – XRD pattern for MgAl-NO₃-LDH.

The XRD pattern of the co-precipitated sample MgIn-NO₃-LDH (Fig. 2) manifested also the presence of hydroxalcite-like phase. The peaks at $d = 0.8027, 0.3952, 0.2676, 0.2368, 0.1981, 0.1583$ and 0.1557 nm can be ascribed to the (003), (006), (009), (015), (018), (110) and (113) reflections of

were detected in this sample.

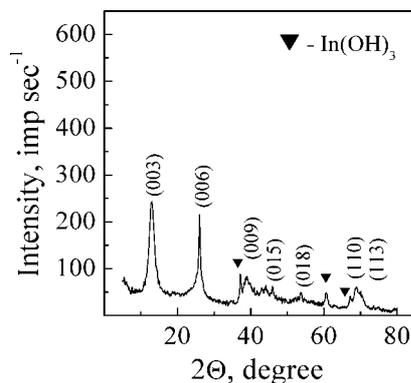


Fig. 2 – XRD pattern for MgIn-NO₃-LDH.

hydroxalcite. It may be seen also that several extra peaks at $d = 0.2786, 0.1769$ and 0.1617 nm appeared, indicating the presence of another phase. These diffraction lines could be attributed to the (220), (420) and (422) reflections of In(OH)₃ additional phase (JCPDS file 16-0161).

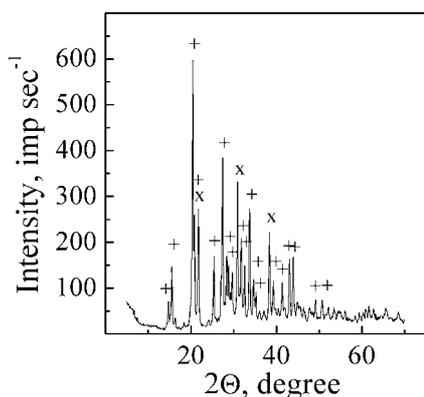


Fig. 3 – XRD patterns for sample MgAl-NO₃: (+) - Mg(NO₃)₂·6H₂O and (x) - Al(NO₃)₃·9H₂O.

The XRD pattern of the evaporated sample MgAl-NO₃ (Fig. 3) represented peaks at $d = 0.6005, 0.5705, 0.4341, 0.4267, 0.3509, 0.3250, 0.3144, 0.3009, 0.2815, 0.2748, 0.2657, 0.2546, 0.2493, 0.2425, 0.2291, 0.2180, 0.2098, 0.2059, 0.1851$ and 0.1798 nm corresponding to the (100), (011), (120), (111), (031), (002), (131), (022), (112), (220), (211), (122), (221), (132), (202), (060), (241), (300) (242) and (213) reflections characteristic of magnesium nitrate hydrate (JCPDS file 42-0211). The peaks at $d = 0.4081, 0.2890, 0.2589$ and 0.2345 nm can be ascribed to the (202), (131), (331) and (314) reflections typical for aluminium nitrate hydrate (JCPDS file 24-0004). The XRD

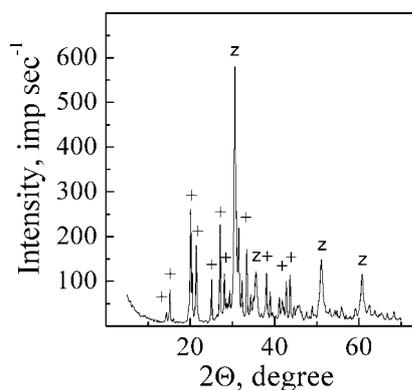


Fig. 4 – XRD patterns for sample MgIn-NO₃: (+) - Mg(NO₃)₂·6H₂O and (z) - cubic In₂O₃.

pattern for the evaporated sample MgIn-NO₃ (Fig. 4) shows also peaks at $d = 0.6154, 0.5816, 0.4410, 0.4137, 0.3548, 0.3285, 0.3173, 0.3041, 0.2836, 0.2771, 0.2679, 0.2611, 0.2521, 0.2361, 0.2310, 0.2193, 0.2112,$ and 0.2071 nm corresponding to the (100), (011), (120), (111), (031), (002), (131), (200), (112), (220), (211), (122), (221), (132), (042), (060), (241), and (300) reflections characteristic of magnesium nitrate hydrate. The diffraction lines at $d = 0.2917, 0.1785$ and 0.1524 nm were observed, corresponding to the (222), (440) and (622) reflections characteristic for cubic In₂O₃ (JCPDS file 06-0416). Obviously, the thermal treatment of evaporated sample MgIn-

NO₃ at $t = 200^\circ\text{C}$ induced the formation of cubic indium oxide. This is an indication for lower thermal stability of MgIn-NO₃ due to the presence of indium in the sample.

It is known that the co-precipitated hydrotalcite-like compounds have rhombohedral 3Rm symmetry with a and c unit cell lattice parameters, where parameter a ($a = 2d_{110}$) corresponds to the distance between neighbouring

cations in the brucite-type layers and increases with the ionic radii of the cations. The parameter c ($c = 3d_{003}$) is three times the distance between adjacent brucite-type layers.⁹ The lattice parameters of the investigated LDHs were calculated by indexing the peaks under the hexagonal crystal system using least-square fitting of the peaks (Table 2).

Table 2

Specific surface area and structural characteristics of the co-precipitated materials

Sample	SSA (m ² g ⁻¹)	Structural characteristics			
		a (nm)	c (nm)	V_{HTL} (nm ³)	$L_{(006)}$ (nm)
MgAl-NO ₃ -LDH	130	0.3052 ± 0.0003	2.4066 ± 0.001	0.197 ± 0.001	5
MgIn-NO ₃ -LDH	80	0.3166 ± 0.0002	2.4082 ± 0.001	0.205 ± 0.002	13
Hydrotalcite*	-	0.3063 ± 0.0001	2.312 ± 0.001	0.188	-

*(Mg₆Al₂(OH)₁₆·4H₂O, JCPDS file 14-0191)

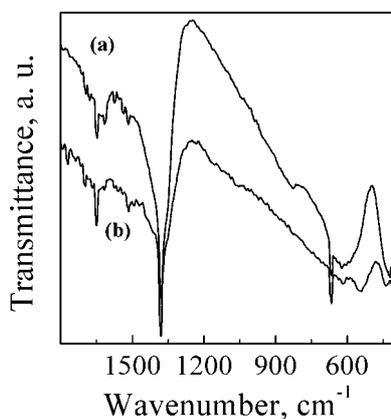


Fig. 5 – IR spectrum for co-precipitated materials: (a) MgAl-NO₃-LDH and (b) MgIn-NO₃-LDH.

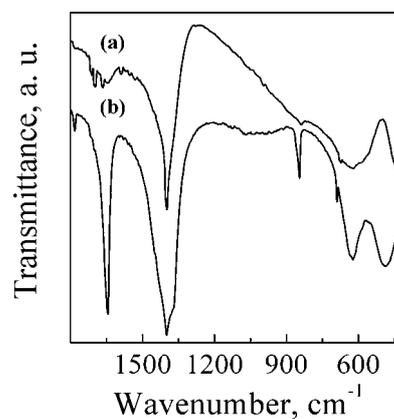


Fig. 6 – IR spectrum for evaporated materials: (a) MgAl-NO₃ and (b) MgIn-NO₃.

The data revealed that the presence of In³⁺ ions led to an increase of the lattice parameters (a and c) and of the total cell volumes (V_t) of the co-precipitated sample. The increase of the parameters a and V_{HTL} may be attributed to the higher octahedral ionic radius of In³⁺ ion ($r = 0.081$ nm) than the corresponding one of Al³⁺ ion ($r = 0.050$ nm).¹³ The reported data of parameter c of both samples were higher than for carbonate containing standard hydrotalcite sample one (Table 2). The differences should be due to larger size of the nitrate ion (0.378 nm) comparative to carbonate one (0.285 nm) as well as to the standing location of nitrate anions in the interlayer space (perpendicular to the brucite layers) instead of the flat location of the carbonate anions (parallel to the brucite layers).

The particle size (L) of the co-precipitated layered samples was estimated from the values of

the full-width at half-maximum of the (006) diffraction peaks by means of the Scherer equation. It can be seen from the Figures 1 and 2, and Table 2 that the particle size of MgIn-NO₃-LDH were greater than of MgAl-NO₃-LDH one for the same Mg²⁺/M³⁺ ratio. The indium presence in Mg-containing LDH induced an increase in the particle size that reflects the surface area decrease (Table 2). The particle size of 17 nm was calculated from (420) reflection for In(OH)₃ phase. It should be noted also that the values of crystallite size for both co-precipitated materials were located in the nano-scale area.

Infrared spectroscopy was used to identify the interlayer anions in the synthesized materials. The IR spectra of both co-precipitated materials (Fig. 5, **a** and **b**) exhibited several bands of low intensity at 1680-1710 and 1480-1520 cm⁻¹, very strong stretching vibrations of ν_3 mode at 1380 and ν_4

mode at 660-670 cm^{-1} . All they are characteristic for NO_3^- ions.¹⁴ A very weak ν_2 mode at 820 cm^{-1} of NO_3^- ions was observed only in the sample MgAl- NO_3 -LDH.¹⁵ Another absorption band corresponding to water molecule bending vibrations, $\delta = 1650 \text{ cm}^{-1}$ was registered. The bands, observed in the low-frequency region, 620–400 cm^{-1} , are assigned to the lattice M–O and M–OH vibrations. These results indicated that the nitrate ions were not exchanged in the interlayer space by CO_3^{2-} ions during the preparation of the co-precipitated materials, confirming the XRD data. The IR spectra of both evaporated materials (Fig. 6, **a** and **b**) were similar to the co-precipitated ones. It may be noticed that the NO_3^- , water molecule and lattice vibration bands were more pronounced in the In-containing sample, MgIn- NO_3 .

CONCLUSIONS

It may be concluded that the preparation procedure and the nature of the trivalent cation influenced the structure and the surface area of the Mg-containing materials prepared either by co-precipitation or by the evaporation methods.

The co-precipitation procedure leads to the formation of layered double hydroxides of hydrotalcite-like structure containing NO_3^- anions in the interlayer space. The NO_3^- anions in the interlayer space were shown that not to have been exchanged in the interlayer space by CO_3^{2-} ions during the preparation procedure.

The presence of Al^{3+} ions induced the formation of a LDH single-phase material of smaller particle size and higher surface area in comparison to that of In^{3+} . The latter cation induced the additional appearance of $\text{In}(\text{OH})_3$ 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.

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