Chemistry for Sustainable Development **21** (2013) 29–38

UDC 54-36:546.924:544.726:544.723.5

Formation of Platinum Centers in Basic Carriers of Layered Double Hydroxide Type

O. B. BELSKAYA[1,2], L. N. STEPANOVA[1], N. N. LEONTYEVA[1], M. O. KAZAKOV[1], T. I. GULYAEVA[1], S. V. CHEREPANOVA[3], A. V. LAVRENOV[1] and V. A. LIKHOLOBOV[1,2]

[1]*Institute of Hydrocarbons Processing, Siberian Branch of the Russian Academy of Sciences,*
Ul. Neftezavodskaya 54, Omsk 644040 (Russia)

E-mail: obelska@ihcp.oscsbras.ru

[2]*Omsk State Technical University,*
Pr. Mira 11, Omsk 644050 (Russia)

[3]*Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences,*
Pr. Akademika Lavrentyeva 5, Novosibirsk 630090 (Russia)

Abstract

Results are reported on studying the interaction of Pt (IV) anionic chloride complexes with layered magnesium-aluminum hydroxides in the course of synthesizing Pt/MgAlO$_x$ catalysts. As the oxide precursors there were layered hydroxides used with different nature of interlayer anions (CO_3^{2-} and OH$^-$) and with Mg/Al ratio ranging within 2–4. The nature of an interlayer of anion is an important parameter affecting the amount of fixed platinum, the composition of surface species and the sites of location thereof in the structure of layered material. In the case of using a hydroxide carrier with the carbonate counterion the fixation of platinum occurs with the participation of the OH groups of hydroxide layers, *via* adsorbing the hydrolyzed forms of the complexes on the surface. The reduction thereof leads to the formation of isometric platinum particles of 2–4 nm in size.

When attaching the platinum complexes to aluminum-magnesium hydroxide with interlayer anions OH$^-$, the precursor of the active component is mainly located in the interlayer space, with further forming the particles of flat morphology 50 nm long and the thickness close to the interlayer distance in the layered carrier (0.75 nm). In the case of varying the Mg/Al ratio, an increase of triply charged aluminum cation causes changing the structural characteristics and adsorption properties of aluminum-magnesium hydroxide to result in the formation of an oxide phase with a more developed surface area and higher pore volume. Increasing the positive charge density and enhancing the electrostatic interaction promote the adsorption of a greater amount of platinum (IV) anionic complexes and a stronger interaction thereof with the hydroxide layers. In the case of changing the Mg/Al ratio from 4 to 2, one can observe increasing the dispersity level of the supported platinum particles and increasing the activity of Pt/MgAlO$_x$ catalysts in the propane dehydrogenation reaction.

Key words: magnesium-aluminum layered hydroxides, platinum, propane dehydrogenation

INTRODUCTION

The Pt(Pd)/MgAlO$_x$ catalysts prepared using magnesium-aluminum layered double hydroxides (MgAl–LDH) as the carrier precursor are being actively studied [1–10], since they are demanded not only in the field of basic catalysis (condensation reactions of alcohols and carbonyl compounds) [3, 4], but also in the conversion of hydrocarbons [5–10]. This, first of all, concerns the dehydrogenation reaction of light alkanes. Increasing the demand for C$_2$–C$_4$ alkenes for the production of polymers determines the interest in the catalytic dehydrogenation to initiate the development of novel catalyst systems. It is known that platinum serves as an active dehydrogenation catalyst, especially in the presence of a modifier, such as Sn, Zn, Ge, Pb and Re [11–19]. To minimize the oligomerization of alkenes formed and to prevent coke formation in the mentioned catalysts one uses non-acidic catalyst species. These include a number of zeolites, alumina modified with cations of alkali, alkaline earth metals and chromium oxide, spinels, [15–25], as well as mixed aluminum-magnesium oxides $MgAlO_x$, produced *via* MgAl–LDH calcination. In this series, the $MgAlO_x$ oxides are most attractive due to a moderate easily controlled basicity thereof, a high stability with respect to oxidative regeneration and the ability to provide a high dispersity level of supported platinum.

The properties of aluminum-magnesium oxides are determined by the composition and arrangement of their precursors, the layered double hydroxides (LDH). It is known that LDH (or hydrotalcite-like compounds) are described by general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$ to consist of brucite-like layers wherein the divalent cations M^{2+} are partially isomorphically substituted by trivalent cations M^{3+} with similar ionic radii (in the case of MgAl–LDH the magnesium cations are substituted by the cations of aluminum). In this case, the excess positive charge of the layers is compensated by hydrated anions A^{n-}, located in the interlayer space. The anions are retained due to the electrostatic interaction, so they exhibit a good mobility being completely interchangeable in the course of ion exchange within the framework of charge equivalence. Factor $x = M^{3+}/(M^{2+} + M^{3+})$. In this case the layered structure exists within a certain range of x values: $0.2 < x < 0.33$. It is important that mixed oxides obtained by means of LDH calcination at a certain temperature, exhibit a "memory effect", *i. e.* they can restore the layered structure in the course of contacting with aqueous solutions. Thus, in the course of using aqueous solutions of precursors for the synthesis of the catalysts the interaction should occur with the material of the layered structure regardless of the nature of the carrier (LDH or a mixed oxide derived therefrom).

Taking into account the features of the structure and properties inherent in the carriers of this type, it is obvious that the patterns of their interaction with the solution of chloroplatinic acid that is commonly used as a precursor in the synthesis of platinum catalysts, should be fundamentally different than in the case of adsorbing the metal complex onto traditional oxide carriers. The main difference consists in the ability to perform exchanging between LDH interlayer anions and anionic complexes of platinum. At the same time, the most of published investigations deal with introducing the compounds of the platinum metals according to water-absorbing capacity using minimum solution amounts and without controlling the processes occurring in the course of fixation [26–28]. The exchange of interlayer anions was considered in solitary papers devoted to studying the anion exchange properties of hydrotalcite-like compounds [28, 29], whereas introducing the precursor of an active catalyst component in the form of anionic species still remains almost unexplored.

It is known that the anion exchange properties of LDH are determined by two main parameters such as the composition of hydroxide layers and the arrangement of interlayer space. The aim of this work consisted in studying the influence of the nature of a LDH interlayer anion (CO_3^{2-} and OH^-) and Mg/Al ratio in the hydroxide layers upon the interaction between the metal complex and the carrier as well as upon the properties of platinum centers under formation.

EXPERIMENTAL

The synthesis of LDH with carbonate counterion (MgAl–CO_3 consisted in the coprecipitation of magnesium and aluminum hydroxides from dilute solutions of nitrates in the course of interaction thereof with solutions containing carbonate and hydroxide ions. Changing the concentration of metals, we obtained LDH with different Mg/Al ratio values. In the course of the synthesis we maintained the constant values of the solution acidity (pH 10) and temperature (60 °C). The resulting precipitate was washed with copious amounts of distilled water, filtered and dried for 16 h at a temperature of 80 °C. For obtaining samples containing predominantly interlayer anions OH^- (MgAl–OH), the original carrier (MgAl–CO_3) was calcined at 600 °C and rehydrated. The calcination temperature was chosen basing on thermal analysis data being corresponding to the completion of the oxide phase formation. In order to perform the investigations using physicochemical methods and sorption measurement, the samples of MgAl–CO_3 and MgAl–OH were preliminary dried at 120 °C for 12 h.

The sorption of $H_2[PtCl_6]$ was performed from the excess of aqueous solutions at a room temperature. The concentration of the solutions was varied depending on the required metal content in the sample. After the adsorption of the metal complex the content of platinum in the solution was monitored by means of a spectrophotometric method, whereas carrier components Mg, Al were monitored using a Varian 710-ES Series ICP OES spectrometer and SHIMADZU AA6300 atomic absorption spectrophotometer.

The XRD investigations were performed by means of a Bruker D8 Advance diffractometer using monochromatic CuK_α radiation in the range of diffraction angles $2\theta = 5–80$ deg. The scanning pitch was equal to 0.05 deg; the signal integration time amounted to 5 s/increment unit.

The measurement of nitrogen adsorption-desorption isotherms at 77.4 K was carried out using an ASAP-2020 volumetric vacuum static unit (Micromeritics). The range of relative equilibrium pressure was equal to $P/P_0 = 10^{-3}–0.996$. The calculations of the specific surface area according to BET (S_{BET}) were performed within the range of relative equilibrium nitrogen vapour pressure $P/P_0 = 0.05–0.2$ basing on the adsorption isotherm. In order to obtain differential characteristic curves for pore size distribution (CPSD) we used a BJH method for the adsorption branch of isotherms. In the calculations we used a cylindrical model for connected pores.

To study the thermal decomposition of LDH samples we used a TG-DTA technique. The measurements were performed using a STA-449C Jupiter unit (Netzsch) in a dynamic mode in air at a heating rate equal to 10 °C/min.

The adsorption of carbon dioxide was measured using a Sorptomatic-1900 automated volumetric vacuum static unit. Before the measurement, the samples were trained under vacuum (10^{-2} mmHg) at 300 °C. In order to determine the presence of the micropores in the samples, we obtained the adsorption isotherms of carbon dioxide at 0 °C within the range of relative pressure values $P/P_0 = 4 \cdot 10^{-5}–0.030$. This measurement is necessary for correctly comparing the samples in the course of determining their capacity with respect to CO_2. To evaluate the basic properties of the carrier we used the adsorption of CO_2 at elevated temperature values. Basing on the adsorption isotherm of carbon dioxide obtained at pressure values up to $P = 1$ atm at the temperature of 30 °C, we calculated the total capacity of the sample with respect to the mentioned gas (physically and chemically adsorbed CO_2). Then we evacuated the sample to 10^{-2} mmHg at the same temperature for 1 h (removal of physically adsorbed molecules) to obtain the second isotherm. From the difference between the amount of adsorbed CO_2 we determined that part of the adsorbed CO_2 which retained on the surface owing to the chemical nature thereof. Further, in order to estimate the strength of basic centers the evacuation stage was carried out at the temperature values equal to 100, 200 and 300 °C.

The ^{195}Pt NMR spectra were obtained by means of an Avance-400 NMR spectrometer (Bruker) using multinuclear sensor SB4 (MAS). The samples under investigation were placed in a 4-mm zirconia rotor and whirled at “magic” angle (54°44′) with a frequency of 10^4 Hz. As an external reference we used an aqueous solution of $H_2[PtCl_6]$ with the concentration of 0.03 mol/L. The pulse duration was equal to 13 μs, the delay time before the digitization being 16 μs, the repetition time amounting to 0.7 s, the width of the “window” being equal to 70 kHz; the number of points per spectrum was equal to 16 000, the total number of pulses being of 4096.

Using the method of temperature-programmed reduction (TPR) we investigated the reduction dynamics of adsorbed complexes employing an AutoChem-2920 unit (Micromeritics). The TPR process after establishing the baseline was performed in the flow of a mixture of 10 vol. % H_2–Ar with heating up to a temperature of 550 °C at a heating rate of 10 °C/min. For the reduced samples, we determined the dispersivity level of platinum using the technique of H_2 pulse chemisorption at a room temperature starting from stoichiometry $[Pt]/[H_2] = 1 : 1$.

The propane dehydrogenation reaction was conducted in a flow-through reactor with a fixed bed catalyst (loading 1 g) at a temperature of 550 °C, atmospheric pressure, molar ratio $H_2/C_3H_8 = 0.25$ and the mass feed rate of 4 $g/(g_{cat} \cdot h)$. The conditions of catalyst pretreatment prior to the reaction involved calcination in air and reduction in a hydrogen flow at 550 °C. The duration of each experiment was equal to 5 h. The product composition was analyzed in an on line mode using a GC-1000 Chromos gas chromatograph equipped with an Rt-Alumina PLOT column (50 m long) and a flame ionization detector.

RESULTS AND DISCUSSION

Effect of interlayer anion nature on the mechanism of metal precursor fixation and the properties of supported platinum

To date, there formed a simplified concept of the mechanisms of interaction between anions and layered metal hydroxides such as hydrotalcite. It is assumed that the anions are involved in the exchange with the interlayer anions and OH groups of brucite-like hydroxide layers to form the ionic-and-covalent bonds with the metal atoms of [30]. The possibility of realizing the anion-exchange mechanism is determined by the nature of the interlayer anion in LDH. As a rule, as a starting material one uses the LDH species those are close in composition to the naturally occurring hydrotalcite containing carbonate ions within the interlayer space. The synthesis thereof using the method of coprecipitation from the corresponding salt solutions by sodium carbonate as a precipitant is simple and exhibits a good reproducibility [30, 31]. At the same time, a low mobility of CO_3^{2-} anions is experimentally observed: they can readily extrude other anions from the interlayer space, but they exhibit a low capacity with respect to the ion exchange replacement.

Attempts were made to explain this fact by forming a network of hydrogen bonds between CO_3^{2-} ions and water molecules [32]. However, the formation of hydrogen bonds is inherent in many anions, which formation could hardly result in completely excluding thereof from the exchange process. Most likely, the observed result could be associated with the interaction between carbonate ions and OH groups of hydroxide layers with the formation of $M-OCO_2^-$ bond. In the course of its formation there remains conserved one of the charges of the anion involved in the compensation of the excess positive charge of the layers. The possibility of mono- and bidentate coordination of carbonate groups was also confirmed the authors of [33] in the study of the processes of dehydration of hydrotalcite interlayer space.

A low exchange capacity of the carbonate form of MgAl–LDH with the ratio Mg/Al = 3 : 1 was determined also with respect to the doubly charged anionic platinum chloride complexes [34]. In this case the reaction with $H_2[PtCl_6]$ does not affect the LDH structural properties characterizing the layered material. However, the chloroplatinate could be fixed in the interlayer space *via* using special techniques. One of them consists in that the $[PtCl_6]^{2-}$ is introduced in the course of the procedure of reducing the layered structure due to the hydration of the mixed oxide in an aqueous solution of the metal complex. In addition, it is possible to preliminarily introduce other anions having good exchange properties [35]. So, we demonstrated earlier that in the case of hydrating the aluminum-magnesium mixed oxide in distilled water, the interlayer space contains mainly ions OH^-, whereas the subsequent replacement thereof by $[PtCl_6]^{2-}$ is close to the maximum possible value. The replacement of interlayer anions CO_3^{2-} by OH^- leads to structural changes in LDH: changing the position of the basal reflex d_{003} inherent in these systems characterizing the layered structure. Reducing the value of d_{003} from 0.78 to 0.77 nm [34] confirms the change in the composition of the interlayer space, namely decreasing the size of the interlayer anion. However, the subsequent sorption of anionic platinum complex leads to increasing the value of d_{003} parameter from 0.77 to 0.79 nm, which is consistent with the idea of fixing the $[PtCl_6]^{2-}$ in the interlayer space *via* anion exchange.

The targeted synthesis and use of layered carriers with different anion-exchange properties allows selectively realizing different mechanisms for fixing the platinum complexes. So, the authors of [34] revealed that in the case of the reaction between $[PtCl_6]^{2-}$ and MgAl–CO_3 the fixation of the metal complex should more likely occur with the participation of the

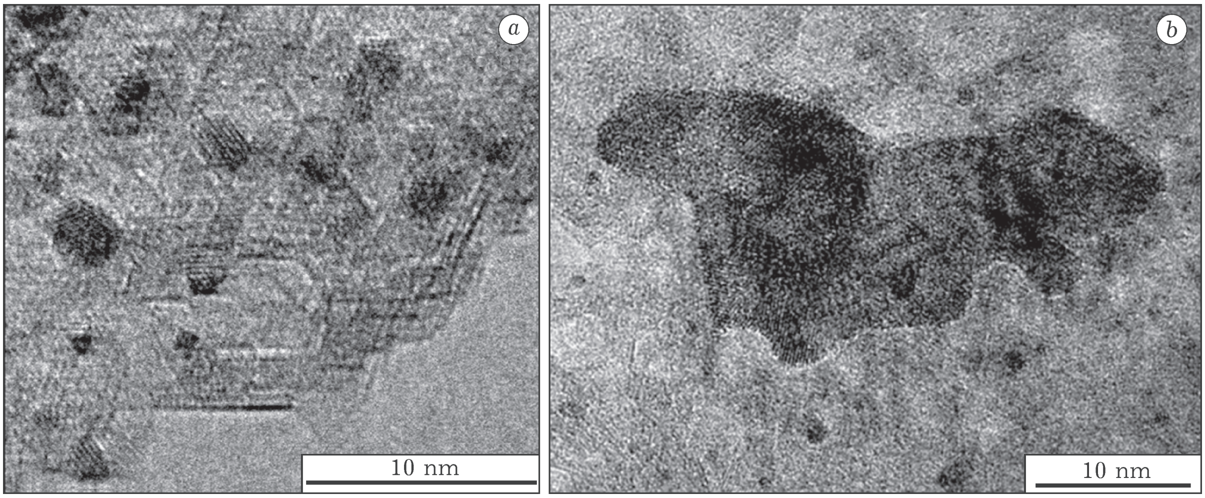

Fig. 1. Electron micrographs of the samples: *a* – Pt/MgAlO$_x$ (precursor of MgAl–CO$_3$) after reduction treatment at 450 °C for 2 h, Pt content 7.8 mass %; *b* – Pt/MgAlO$_x$ (precursor MgAl–OH), the same treatment, Pt content 10.2 mass % [34].

OH groups of the hydroxide layers to form the hydrolyzed forms of platinum complexes on the surface. As the result, after the reduction treatment there occurs the formation of isometric platinum particles with the sizes of 2–4 nm (Fig. 1, *a*) located on the surface of the aluminum-magnesium oxide.

In the course interaction between chloroplatinate and MgAl–OH, the interlayer OH$^-$ ions are readily replaced by doubly charged complex anions $[PtCl_6]^{2-}$, whereas the reduced samples with an insignificant fraction of small isometric particles contain the platinum mainly in the structure of larger particles with flat morphology (see Fig. 1, *b*). This fact indicates that the formation of the platinum particles occurs under tight conditions of layered structure. The length of the flat particles amounts to 50 nm, whereas the thickness thereof is close to the interlayer distance (d_{003} = 0.75 nm) in the original manganese-aluminum hydroxide MgAl–OH.

Revealing the differences in the mechanisms of fastening the metal complexes on MgAl–LDH in the hydroxide and carbonate forms was performed using a ^{195}Pt MAS NMR technique. It is known that this method allows one to obtain information concerning the composition of adsorbed complexes and the nature of their interaction with the surface [36, 37]. In the course of studying the $[PtCl_6]^{2-}$ complexes, adsorbed on the surface of the carrier, it was found that the NMR signals from ^{195}Pt could be observed only in the case when the octahedral symmetry of the complexes under adsorption is retained or slightly distorted. So, with coordination fixing the complex on aluminum oxide, when one or more of chloride ligands in the $[PtCl_6]^{2-}$ anion are replaced by the hydroxyl groups of the carrier, one can observe either significantly decreasing the intensity or broadening the peaks, or the fact that NMR signals are not detected. Just such a situation occurs in the course of adsorbing the complexes on MgAl–LDH with carbonate counterions. On the surface there are hydrolyzed forms of platinum complexes (according to ESDR [34]), whereas ^{195}Pt NMR signals of these complexes were not obtained. This result confirms the assumption concerning the coordination fixation of platinum complexes with the participation of OH groups inherent in hydroxide layers.

At the same time, in the case of using MgAl–OH as a carrier, the spectrum exhibits a strong peak corresponding to chloride complexes $[PtCl_6]^{2-}$, and a signal of low intensity, whose position is inherent in monosubstituted chloro-hydroxo complexes such as $[PtCl_5(OH)]^{2-}$ [36, 37] (Fig. 2). Consequently, the bond type realized between the complexes of platinum (IV) and the surface of the carrier does not cause any noticeable changes in the chemical composition of the complex and the geometry

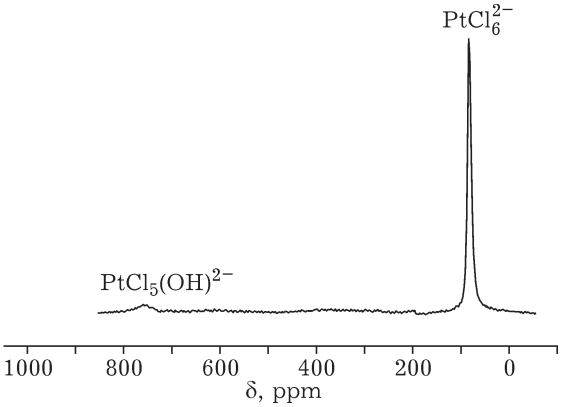

Fig. 2. ^{195}Pt MAS NMR spectrum of platinum (IV) complexes adsorbed on MgAl–OH. The sample was dried at 25 °C for 48 h, platinum content 10 mass %.

distortion; thus the mentioned bond type could be attributed to weak electrostatic interaction.

It should be noted that the differences in the mechanism of the fixation and the localization of the precursor on the MgAl–LDH with interlayer anions OH^- and CO_3^{2-} result in the formation platinum centers those differ from each other in the dispersity level of platinum and catalytic properties. The dispersity level of the supported platinum was determined for the samples of 0.3Pt/$MgAlO_x$ (Pt content being of 0.3 mass %) with equal chemical composition, differing only in the arrangement of the hydroxide precursor of the carrier.

The samples were preliminary calcined at 550 °C and reduced in hydrogen at 550 °C. From data on the chemisorption of hydrogen molecules one can see that the platinum particle dispersity level is equal to 73 % for sample 0.3Pt/$MgAlO_x(CO_3^{2-})$, prepared using $MgAl–CO_3$, decreasing to 23 % in the case of mainly fixing the chloroplatinate in the interlayer space of the support with the use of MgAl–OH. In this case, at a lower platinum dispersity level the sample of 0.3Pt/$MgAlO_x(OH^-)$ has a higher dehydrogenating activity (Fig. 3). Moreover, the mentioned catalyst is more stable. So, in the presence of the sample 0.3Pt/$MgAlO_x(OH^-)$, the conversion level of propane demonstrates a 20.5 rel. % decrease for 5 h of operation, whereas the sample 0.3Pt/$MgAlO_x(CO_3^{2-})$ exhibits a 33.2 rel. % decrease of this value.

Thus, the choice of the interlayer anion allows realizing the mechanism necessary for the interaction between the metal complex and carrier, and changing the region of localizing the precursor of active component in the course of adsorption. As a result, with the same chemical composition of Pt/$MgAlO_x$ samples one could obtain the particles of supported platinum fundamentally different in size, morphology, and catalytic properties under the model reaction conditions.

Effect of Mg/Al ratio in layered double hydroxides on the formation of platinum centers in Pt/$MgAlO_x$ catalyst

The ratio between doubly and triply charged cations in the hydroxide layers determines the capacity of the interlayer space and the strength of interaction between hydroxide layers and interlayer anions. In order to study the adsorption of the platinum complexes we prepared magnesium-aluminum hydroxide in the carbonate form $MgAl–CO_3$ with further converting them into MgAl–OH *via* the stage of mixed oxide hydration in water. The ratio be-

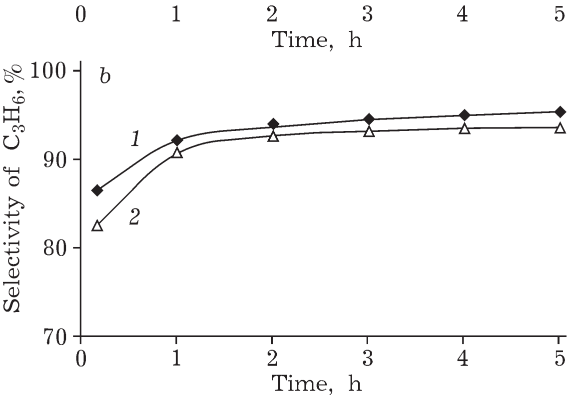

Fig. 3. Conversion level of propane (*a*) and the selectivity level of propylene formation (*b*) for the samples of 0.3Pt/$MgAlO_x(CO_3^{2-})$ (*1*) and 0.3Pt/$MgAlO_x(OH^-)$ (*2*). Platinum content 0.3 mass %.

TABLE 1

Structural characteristics of MgAl–LDH samples containing different counterions under varying the ratio between cations

Samples	Mg/Al	d_{003}, nm	a, nm	c, nm	L_a, nm	L_c, nm
MgAl–CO_3	2.2	0.76	0.304	2.28	19.8	13.4
MgAl–CO_3	3.1	0.783	0.306	2.35	16.7	12.1
MgAl–CO_3	4.0	0.789	0.307	2.38	11.9	8.1
MgAl–OH	2.2	0.756	0.305	2.28	13.2	8.0
MgAl–OH	3.1	0.759	0.308	2.32	8.4	6.5
MgAl–OH	4.0	0.779	0.308	2.36	7.8	5.7
[$PtCl_6$]/MgAl–OH*	2.2	0.766	0.305	2.29	15.0	9.0
[$PtCl_6$]/MgAl–OH*	3.1	0.778	0.307	2.33	11.0	2.0
[$PtCl_6$]/MgAl–OH*	4.0	0.798	0.310	2.38	–	–

*Pt content in the [$PtCl_6$]/MgAl–OH samples is equal to 12 mass % as calculated for the sample calcined at 600 °C.

tween the metals M^{2+}/M^{3+} was varied within the range of 2–4. Changing the Mg^{2+}/Al^{3+} ratio resulted in considerable changing the structural characteristics of LDH. From Table 1 one can see that increasing the Mg fraction results in significant changing the basal reflexes d_{003} and d_{006} towards smaller angles and, consequently, in an increase in the parameter c. This could be connected with decreasing the electrostatic interaction between the positively charged brucite-like layers and the interlayer spaces [30]. In addition, the reflex d_{110} is shifted towards lower angles, resulting in increasing the lattice parameter a due to the difference in the ionic radii values inherent in magnesium (0.078 nm) and aluminum (0.057 nm). Increasing the magnesium content also promotes reducing the size of the crystallites in all the directions, which results in increasing the half-width both basal reflexes d_{003}, d_{006}, and reflexes d_{110}, d_{113}. This tendency is inherent in LDH both in the carbonate and in the hydroxide forms (see Table 1).

The M^{2+}/M^{3+} ratio (hydroxide layer charge) in LDH determines to a considerable extent the formation of the pore space in the oxide phase occurring after high temperature processing, and as well as acid-base properties thereof. With decreasing the strength of interaction between the hydroxide layers and interlayer anions, increasing the magnesium content results in a decrease of the specific surface area and total

TABLE 2

Main textural characteristics of the magnesium aluminum oxide samples under investigation according to nitrogen adsorption. Preliminary calcination of the samples at 600 °C

Samples	Mg/Al	S_{sp}, m^2/g	$V_{ads,}$ cm^3/g	D, nm
$MgAlO_x(CO_3)$	2.2	264	1.02	15.4
$MgAlO_x(CO_3)$	3.1	242	0.63	10.4
$MgAlO_x(CO_3)$	4.0	171	0.38	8.9
$MgAlO_x(OH)$	2.2	270	0.51	7.5
$MgAlO_x(OH)$	3.1	220	0.29	5.3
$MgAlO_x(OH)$	4.0	149	0.30	8.0

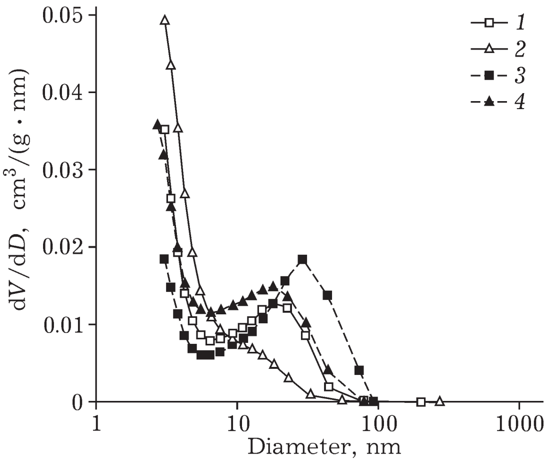

Fig. 4. Pore size distribution curves plotted basing on the adsorption branch for $MgAlO_x$ samples with Mg/Al ratio = 2 : 1 (*1*, *3*) and 3 : 1 (*2*, *4*) obtained from precursors MgAl–LDH with counterions OH^- (*1*, *2*) and CO_3^{2-} (*3*, *4*). The samples were calcined at 600 °C; pore diameter is presented in logarithmic coordinates.

pore volume of the aluminum-magnesium oxides (Table 2), whereas the maxima of pore size distribution exhibit shifting towards smaller values (Fig. 4).

So, the calcination of MgAl?CO_3 sample with the ratio of Mg/Al = 2 : 1 leads to the formation of an oxide phase characterized by a wide pore size distribution within the range of 10–100 nm (the fraction of mesopores within this range being equal to 90 %) with a pronounced maximum at 29 nm (see Fig. 4). Increasing the ratio of Mg/Al up to 3 : 1 results in decreasing the fraction of large mesopores, the main fraction of pores occurring within the range of 6–40 nm (70 %) with a maximum at 18 nm. When Mg/Al = 4 : 1 one can observe a more uniform PSD: the fraction of the mesopores within the range less than 30 nm is equal to 70–80 % with the maxima at about 13 and 4 nm. In the case when the OH anions (with a smaller size as compared to anions CO_3^{2-}) prevail in the interlayer space, the value of a number of texture parameters exhibit a decrease (see Table 2).

However, the tendency of M^{2+}/M^{3+} influencing upon them is the same (see Fig. 4).

The effect of Mg/Al ratio on the basic properties of magnesium aluminum oxides was studied using a method of CO_2 adsorption [38, 39]. From Fig. 5 one could see that a higher capacity with respect to carbon dioxide is exhibited by a sample with the maximum content of magnesium (Mg/Al = 4 : 1). Although with increasing the temperature of evacuation the total amount of surface centers capable of retaining CO_2 exhibits a decrease, however even under the most severe conditions of evacuation (300 °C) there are some centers of strong chemisorption. For the samples with the ratio of Mg/Al = 2 : 1 and 3 : 1 the number of such centers is almost equal, whereas the sample with Mg/Al = 4 : 1, demonstrates this value to be four times higher. Comparing the TPD for CO_2 and the IR spectroscopy data demonstrated [40] that the processing temperature below 100 °C provides completely removing the bicarbonate species adsorbed on weakly basic centers. At 300 °C, strongly adsorbed bidentate forms of CO_2 molecule are removed.

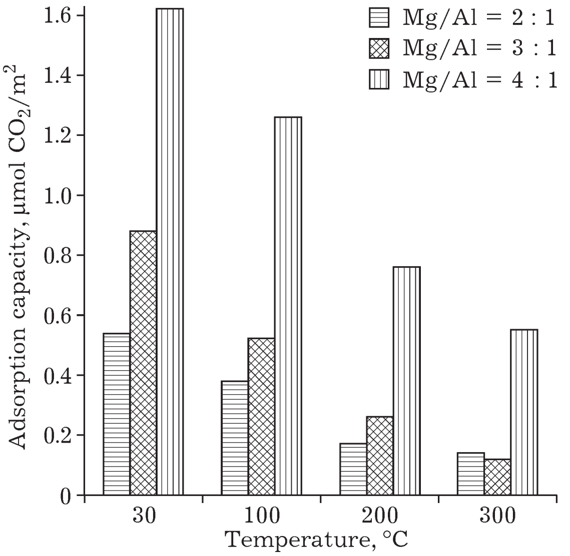

Fig. 5. Adsorption capacity with respect to CO_2 for $MgAlO_x$ samples with different Mg/Al ratio values. Adsorption temperature 30 °C; desorption temperature: 30, 100, 200, 300 °C.

Introducing the platinum complexes to the structure of LDH was carried out using MgAl–OH with different Mg/Al ratio values. It is demonstrated that the exchange with the interlayer anions OH^- promotes a considerable increase in the interplanar spacing of LDH (see Table 1). Increasing the interplanar distance with decreasing the fraction of aluminum (and, consequently, the excess positive charge) and with a close content of the metal complex within the layers might indicate decreasing the strength of interaction between the metal complex and the carrier. This effect can further influence upon the process of forming the supported platinum particles.

So, using the method of TPR it has been found that increasing the proportion of aluminum from 0.2 (Mg/Al = 4 : 1) to 0.33 (Mg/Al = 2 : 1) and the positive charge value for the layer, the platinum reduction process becomes complicated: the maximum of the TPR peak exhibits shifting from 205 to 240 °C. In this case,

TABLE 3

Platinum dispersity level (*D*) according to H_2 chemisorption for Pt/$MgAlO_x$ samples with different Mg/Al ratio values. Platinum content 0.3 mass %

Samples	Mg/Al	*D*, %
0.3Pt/$MgAlO_x$(OH)	2 : 1	44
0.3Pt/$MgAlO_x$(OH)	3 : 1	33
0.3Pt/$MgAlO_x$(OH)	4 : 1	21

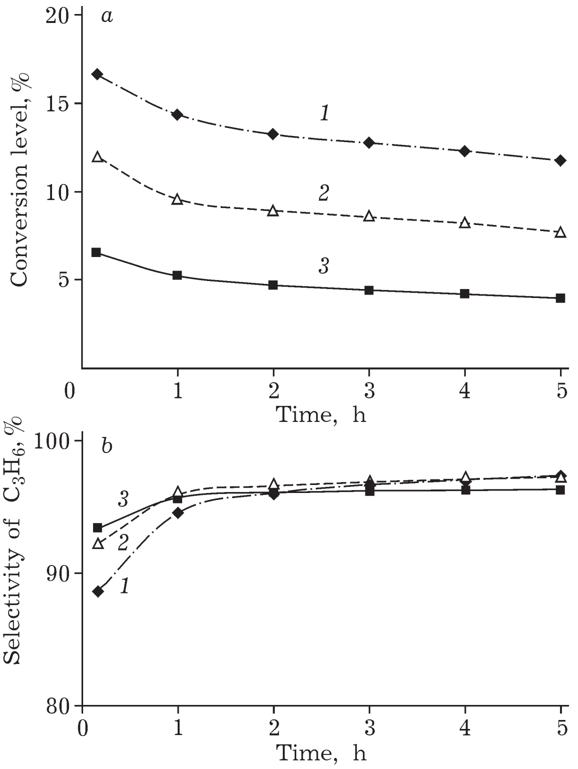

Fig. 6. Conversion level of propane (*a*) and the selectivity level of propylene formation (*b*) for 0.3Pt/$MgAlO_x$ samples with different Mg/Al ratio values: 2 : 1 (*1*) 3 : 1 (*2*) 4 : 1 (*3*).

despite the higher reduction temperature, enhancing the interaction between the metal complex and the carrier leads to the formation of more dispersed platinum particles (Table 3). The difference in the dispersity level and determines the difference in the activity of the samples obtained. From Fig. 6 it follows that the highest values of the conversion level during the entire time of the experiment are observed for the sample with the maximum content of aluminum with $D = 44$ % (see Fig. 6, *a*). Decreasing the dispersity level and the number of reaction centers, the activity of the samples exhibits a decrease.

The selectivity in the formation of different reaction products for the samples under investigation is different only within the initial period of the experiment (during the first hour of the reaction). This sample with the ratio Mg/Al = 2 : 1 having less pronounced basic properties is characterized by a high activity in non-target C?C bond hydrogenolysis reactions with the formation of methane, ethane and ethylene. However, under steady-state conditions the selectivity level values for the samples under investigation with respect to forming the target product (propylene) become comparable to be equal to 96–97 % (see Fig. 6, *b*).

CONCLUSIONS

A synthesis of layered aluminum-magnesium hydroxides with different Mg/Al ratio values and different nature of interlayer anion was performed. The differences revealed in the basic structural parameters of LDH are associated both with the nature of a counterion and with the ratio between two- and triply charged cations in the hydroxide layers. In the case of the transition from LDH in the carbonate form (MgAl–CO_3) tor LDH in the hydroxide form (MgAl–OH) at the same ratio Mg/Al = 3 : 1, the main result consists in reducing the size of the interlayer anion, which leads to reducing the interlayer distance. Good exchange properties inherent in OH^- counterion promote fixing the chloride complexes of platinum (IV) in the interlayer space of LDH *via* the electrostatic interaction with the brucite-like layers. The subsequent platinum reduction under the tightened conditions of the layered structure leads to the formation of platinum centers characterized by a higher activity and stability in the course of the model reaction of propane dehydrogenation.

Increasing the fraction of aluminum in hydroxide layers causes increasing the positive charge density and enhancing the electrostatic interaction. Consequently, there is a decrease in the interlayer distance in the presence of interlayer anions of the same nature. From the MgAl–LDH samples with a high content of aluminum and a high content of anions in the interlayer space, an oxide phase with the most developed surface area and pore volume is formed. Furthermore, increasing the proportion of aluminum in the MgAl–OH composition promotes the anionic exchange to replace the interlayer anions of the carrier by anionic platinum (IV) complexes. In this case, not only the adsorption of a great amount of complexes occurs, but also a more tight interaction thereof with the layered carrier. Thereby, the subsequent reduction treatment leads to the fact that much more dispersed platinum particles are formed. As the result, the 0.3Pt/MgAlO$_x$ catalysts with the ratio Mg/Al ~ 2 : 1 exhibit the highest dehydrogenation activity in the series of the samples studied.

Acknowledgements

The authors thank O. V. Maevskaya for the participation in the synthesis of the samples, G. G. Savelyeva for performing the adsorption measurements, V. P. Talzi for studying the samples by means of ^{195}Pt MAS NMR, N. V. Antonicheva for performing thermal analysis, as well as T. B. Kireeva and A. V. Shilova for the elemental analysis of the samples synthesized.

REFERENCES

1 Beaudot P., De Roy M. E., Besse J. P., *J. Solid State Chem.*, 177 (2004) 2691.
2 Basile F., Fornasari G., Gazzano M., Vaccari A., *Appl. Clay Sci.*, 16 (2000) 185.
3 Narayanan S., Krishna K., *Appl. Catal. A*, 174, 1–2 (1998) 221.
4 Lorret O., Morandi S., Prinetto F., Ghiotti G., Tichit D., Durand R., Coq B., *Micropor. Mesopor. Mater.*, 103 (2007) 48.
5 Kazansky V. B., Borovkov V. Yu., Derouane E. G., *Catal. Lett.*, 19 (1993) 327.
6 Albertazzi S., Busca G., Finocchio E., Glöckler R., Vaccari A., *J. Catal.*, 123 (2004) 372.
7 Galvita V., Siddiqi G., Sun P., Bell A. T., *J. Catal.*, 271 (2010) 209.
8 Sun P., Siddiqi G., Chi M., Bell A. T., *J. Catal.*, 274 (2010) 192.
9 Siddiqi G., Sun P., Galvita V., Bell A. T., *J. Catal.*, 274 (2010) 200.
10 Armendáriz H., Guzmán A., Toledo J. A., Llanos M. E., Vázquez A., Aguilar-Rios G., *Appl. Catal.* A, 211 (2001) 69.
11 Buyanov R. A., Pakhomov N. A., *Kinet. Catal.*, 42, 1 (2001) 64.
12 Bocanegra S. A., de Miguel S. R., Borbath I., Margitfalvi J. L., Scelza O. A., *J. Mol. Catal. A*, 301 (2009) 52.
13 Yu C., Xu H., Ge Q., Li W., *J. Mol. Catal. A*, 266 (2007) 80.
14 Yu C., Ge Q., Xu H., Li W., *Appl. Catal. A*, 315 (2006) 58.
15 Silvestre-Albero J., Sanchez-Castillo M. A., He R., Sepúlveda-Escribano A., Rodríguez-Reinoso F., Dumesic J. A., *Catal. Lett.*, 74, 1–2 (2001) 17.
16 Nawaz Z., Tang X., Zhang Q., Wang D., Fei W., *Catal. Commun.*, 10 (2009) 1925.
17 Katranas T. K., Triantafyllidis K. S., Vlessidis A. G., Evmiridis N. P., *Catal Lett.*, 118 (2007) 79.
18 Zhang S., Zhou Y., Zhan Y., Huang L., *Catal. Lett.*, 135 (2010) 76.
19 Casella M. L., Siri G. J., Santori G. F., Ferretti O. A., *Langmuir*, 16 (2000) 5639.
20 Gascyn J., Téllez C., Herguido J., Menéndez M., *Appl. Catal. A*, 248 (2003) 105.
21 Rombi E., Cutrufello M. G., Solinas V., De Rossi S., Ferraris G., Pistone A., *Appl. Catal. A*, 251 (2003) 255.
22 Lobera M. P., Tellez C., Herguido J., Menéndez M., *Appl. Catal. A*, 349 (2008) 156.
23 Bocanegra S. A., Castro A. A., Guerrero-Rurэz A., Scelza O. A., de Miguel S. R., *Chem. Eng. J.*, 118 (2006) 161.
24 Bocanegra S. A., Guerrero-Ruiz A., de Miguel S. R., Scelza O. A., *Appl. Catal. A*, 277 (2004) 11.
25 Bocanegra S. A., Ballarini A. D., Scelza O. A., de Miguel S. R., *Mater. Chem. Phys.*, 111 (2008) 534.
26 Fornasari G., Glockler R., Vaccari A., *Appl. Clay Sci.*, 29 (2005) 258.
27 Gandao Z., Coq B., Menorval L. C., Tichit D., *Appl. Catal. A: Gen.*, 147 (1996) 395.
28 Lukashin A. V., Chernysheva M. V., Vertegel A. A., Tretyakov Yu. D., *Dokl. AN*, 388 (2003) 200.
29 Miyata S., *Clays Clay Minerals*, 31, 4 (1983) 305.
30 Cavani F., Trifiro Fr., Vacari A., *Catal. Today*, 11 (1991) 173.
31 He J., Wei M., Li B., Kang Y., Evans D. G., Duan X., *Struct. Bond*, 119 (2006) 89.
32 Gutmann N., Muller B., *J. Solid State Chem.*, 122, 1 (1996) 214.
33 Costa D. G., Rocha A. B., Souza W. F., Chiaro S. S. X., Leitaão A. A., *J. Phys. Chem.*, 116 (2012) 13679.
34 Belskaya O. B., Gulyaeva T. I., Leontyeva N. N., Zaikovskii V. I., Larina T. V., Kireeva T. V., Doronin V. P., Likholobov V. A., *Kinet. Katal.*, 52, 6 (2011) 899.
35 Forano C., Hibino T., Leroux F., Taviot-Guého C., in: Handbook of Clay Science, in F. Bergaya, B. K. G. Theng and G. Lagaly (Eds.), vol. 1, chapter 13.1, Elsevier, Amsterdam, 2006, pp. 1021–2095.
36 Shelimov B. N., Lambert J.-F., Che M., Didillon B., *J. Catal.*, 185, 2 (1999) 462.
37 Shelimov B. N., Lambert J.-F., Che M., Didillon B., *J. Molec. Catal. A: Chem.*, 158, 1 (2000) 91.
38 Nam S. S., Kim H. K., Ishan G., Choiane M. J., Lee K. W., *Appl. Catal. A*, 179 (1999) 155.
39 Salvador R., Casal B., Yates M., Martín-Luengo M. A., Ruiz-Hitzky E., *Appl. Clay Sci.*, (2002) 103.
40 Di Cosimo J. I., Díez V. K., Xu M., Iglesia E., Apesteguía C. R., *J. Catal.*, 178 (1998) 499.