Effect of the Nature of the Active-Component Precursor on the Properties of Pt/MgAlO_x Catalysts in Propane and *n*-Decane Dehydrogenation¹

L. N. Stepanova^{*a*, *b*, *, O. B. Belskaya^{*a*, *c*}, and V. A. Likholobov^{*a*, *c*, *d*}}

^aInstitute of Hydrocarbons Processing, Siberian Branch, Russian Academy of Sciences, Omsk, 644040 Russia ^bOmsk State University, Omsk, 644077 Russia ^cOmsk State Technical University, Omsk, 644050 Russia ^dOmsk Research Center, Siberian Branch, Russian Academy of Sciences, Omsk, 644024 Russia *e-mail: Lchem@yandex.ru Received September 22, 2016

Abstract—The $Pt/MgAlO_x$ catalysts, in which a mixed aluminum—magnesium oxide obtained by the heat treatment of corresponding layered double hydroxides was used as a support, were studied. The effects of the

nature of active-component precursors ($[PtCl_6]^{2-}$, $[PtCl_4]^{2-}$, and $[Pt_3(CO)_6]_6^{2-}$), and the Mg/Al ratio in the support on the anchoring of complexes, the disperse state of platinum, and the properties of the obtained catalysts in the reactions of propane and *n*-decane dehydrogenation were found.

Keywords: platinum catalysts, mixed oxides, anchoring of the anionic complexes of platinum, propane dehydrogenation, *n*-decane dehydrogenation

DOI: 10.1134/S0023158417040188

INTRODUCTION

The dehydrogenation reactions of light and higher alkanes are of great industrial importance because they make it possible to obtain alkenes as intermediate products for their further use in the production of polymers and synthetic detergents [1-3]. The development of new catalytic systems with high selectivity for the formation of alkenes is of considerable current interest because of the growing demand for these products. Among the currently available catalysts, systems based on platinum in which the active metal is fixed on a nonacid support are most promising [4-6]. Supports with basic properties are used in order to decrease the contribution of cracking, isomerization, and coke formation side reactions, which occur on acid sites. The formation of an optimum disperse and electronic state of the supported metal is very important for the preparation of active and selective catalysts because the target dehydrogenation reaction occurs on the particles of platinum. An increase in the dispersion of Pt particles leads to an increase in the dehydrogenating activity. Furthermore, the disperse and electronic state of the active metal influences the strength

¹ This paper is based on the proceedings of the V All-Russian Scientific Youth School and Conference "Chemistry under the Sigma Sign: Studies, Innovations, and Technologies" (Omsk, May 15–20, 2016). of the adsorption of reagents. In this case, a decrease in the strength of the adsorption of target products (alkenes) decreases the probability of their subsequent dehydrogenation with the formation of diene hydrocarbons and coke-forming products [7-9].

Both the nature of precursor compounds and their interactions with the support have an effect on the formation and properties of platinum centers. In this work, we studied platinum catalysts supported onto mixed aluminum-magnesium oxides MgAlO_x, which were obtained by the calcination of corresponding layered double hydroxides (LDHs). These oxide supports possess moderate basicity and high specific surface areas [10], and their properties can be easily regulated by changing the composition of their precursors, i.e., LDHs. The LDHs are inorganic materials whose layers include the cations of different-valence metals and anions, which compensate for their positive charge, and water molecules are located between the layers [11]. The basic, adsorptive, textural, and structural properties of LDHs and the oxides obtained from them can be regulated by changing the nature of metals in the layers and a ratio between them and the nature of interlayer anions. In this work, we synthesized LDHs with Mg/Al = 2, 3, and 4 for varying the acid-base and adsorptive properties of the supports.

Complex compounds with different compositions and the oxidation states of the central atom were chosen as the precursors of platinum: anionic chloro complexes of Pt(IV) and Pt(II), namely, $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$, and the carbonyl complex $[Pt_3(CO)_6]_6^{2-}$, containing Pt(0). The octahedral chloro complexes of Pt(IV) and the square-planar chloro complexes of Pt(II) from aqueous solutions were anchored on the surface by anion exchange with the interlayer anions of LDHs (intercalation into the interlayer space). Carbonyl complexes were deposited onto the surface of the preliminarily formed mixed oxides from solutions in acetone without changes in the support structure (anchoring on the external surface). Different activecomponent precursor compounds and different methods of their supporting made it possible to ensure different strengths of metal-support interactions and to reveal the effect of the above differences on the formation and properties of platinum particles.

The aim of this work was to study the effect of the nature of the complex compounds of platinum immobilized on aluminum—magnesium supports with different Mg/Al ratios on the properties of $Pt/MgAlO_x$ catalysts in the dehydrogenation reactions of propane and *n*-decane.

EXPERIMENTAL

The MgAl-LDH samples were obtained by a traditional coprecipitation method using the gradual addition of a solution containing magnesium and aluminum nitrates to a solution of sodium carbonate at a constant value of pH 10 and a temperature of 60°C with the subsequent aging of the suspension at 60°C for 18 h [12]. LDHs with the predominance of carbonate anions in the interlayer space were obtained after washing, filtration, and drying at 80°C. LDHs with the predominant occurrence of hydroxide anions in the interlayer space (an "activated" form) were prepared in order to exchange the interlayer anions for the anions of metal complexes. For this purpose, the synthesized MgAl-LDH was calcined at 550°C (to obtain a mixed oxide $MgAlO_x$) and then rehydrated in distilled water [13].

The X-ray diffraction analysis of LDHs was performed on a D8 Advance diffractometer (Bruker, Germany) in parallel Cu K_{α} radiation in a range of 2 θ angles from 5° to 80° with a scan step of 0.05° and a signal integration time of 5 s at each step.

The textural characteristics of MgAl-LDH were studied after preliminary heat treatment at 550°C. The adsorption–desorption isotherms of nitrogen at 77.4 K were obtained on an ASAP-2020 volumetric vacuum system (Micromeritics, United States). The range of relative equilibrium pressures was from 10^{-3} to 0.996 P/P_0 . Specific surface areas (S_{BET}) were determined by the BET method in a range of the rela-

tive equilibrium pressures P/P_0 of nitrogen vapor from 0.05 to 0.25 based on the adsorption isotherm. In the calculation of S_{BET} , the molecular area of nitrogen in a filled monolayer was taken to be 0.162 nm². The adsorption pore volume (V_{ads}) was measured based on the adsorption of nitrogen at $P/P_0 = 0.990$, assuming that the adsorbate density was equal to the density of normal liquid, namely, 0.02887 mol/cm³. The average pore diameter (d) was evaluated according to the formula $d = 4V_{\text{ads}}/S_{\text{sp}}$.

The aqueous solutions of hexachloroplatinum acid were prepared from the crystal hydrate $H_2[PtCl_6] \cdot 6H_2O$ (chemically pure, Aurat). Tetrachloroplatinum acid ($H_2[PtCl_4]$) was obtained by the reduction of $H_2[PtCl_6]$ by hydrazine chloride [N_2H_6]Cl₂ [14]. For this purpose, a stoichiometric amount of hydrazine chloride was slowly added to an aqueous solution of $H_2[PtCl_6]$; then, the resulting solution was heated in a water bath for 1 h until the complete termination of effervescence.

The carbonyl complexes of platinum $[Pt_3(CO)_6]_6^{2-}$ were synthesized by the reduction of a solution of chloroplatinic acid with carbon monoxide [15]. For this purpose, 100 mL of an aqueous solution of H₂[PtCl₆] with a platinum concentration of 2 mg/mL was placed in a two-neck round-bottom flask with a volume of 250 mL equipped with a magnetic stirrer after blowing argon through the flask. Next, the system was filled with carbon monoxide with intense stirring. In the course of the synthesis, the entire system was blown with a flow of CO for the removal of the resulting CO₂. The cherry-red precipitate of the carbonyl complex of platinum was separated from the aqueous solution by filtration; thereafter, it was dissolved in acetone.

The concentrations of magnesium and aluminum in the solutions and solid samples were determined by inductively coupled plasma atomic emission spectroscopy on a Varian 710-ES instrument (Varian, United States) and by atomic absorption spectroscopy on an AAS 6300 SHIMADZU instrument (Shimadzu, Japan). The platinum content of the solid samples was evaluated after their dissolution in a mixture of acids. Platinum concentrations in solutions were measured on a PE-5400VI spectrophotometer (Ekokhim, Russia).

The chloro complexes of platinum $([PtCl_4]^{2-}$ and $[PtCl_6]^{2-})$ were immobilized on LDHs in an "activated" form (a fraction of 0.25–0.5 mm) at room temperature from an excess of an aqueous solution with the ratio support : solution = 1 : 25 by means of anion exchange between the interlayer hydroxide anions and the anions of metal complexes [16]. The adsorption time was 1 h. After the supporting of a complex, the sample was washed with distilled water and dried in air. The carbonyl complexes of platinum were anchored on

the mixed oxides at room temperature from an excess of an acetone solution with support : solution = 1:25. The support was preliminarily evacuated and blown with argon for the removal of oxygen from the pore space. The adsorption time was 20 min; thereafter, the support with the adsorbed precursor was separated from the solution by filtration, washed with acetone, and dried in air.

Individual weighed portions with the weight ratio support : solution = 1 : 40 were used for obtaining the adsorption isotherms of the chloro complexes of Pt(IV) and Pt(II) on an "activated" form of MgAl-LDH. In each particular case, the adsorption time was 24 h. It was preliminarily found that this time is sufficient for adsorption equilibration. Then, the support with the adsorbed complex was separated from the solution by filtration. The concentration of solutions was varied from 1 to 40 mmol/L. The platinum content of the stock solutions and solutions after metal complex adsorption was monitored by spectrophotometry.

The electronic diffuse-reflectance spectra (DRES) of the supported platinum complexes were measured on a UV-2501PC spectrophotometer (Shimadzu, Japan) with an ISR-240A attachment in a range of 11000– 54000 cm^{-1} . BaSO₄ was used as a reference sample. The experimental spectra were represented in the Kubelka–Munk function–wavenumber coordinates.

The composition of the platinum complexes supported on LDHs and the metal complex-support interactions were evaluated by ¹⁹⁵Pt magic angle spinning NMR (MAS NMR) spectroscopy. The spectra of solid samples were obtained on an Avance-400 spectrometer (Bruker, Germany) with an SB4 (MAS) multinuclear sensor at a Larmor frequency of 86 MHz. The test samples were placed in 4 mm rotors of zirconium oxide and spun at a magic angle $(54^{\circ}44')$ at a frequency of 10^4 Hz. The pulse duration was 13 µs; the delay time before digitization was 16 us; the pulse repetition time was 0.7 s; the window width was 70 kHz; the number of points per spectrum was 16 000; and the total number of pulses was 4096. An aqueous solution of $H_2[PtCl_6]$ with a concentration of 0.03 mol/L was used as an external standard.

The chemisorption of hydrogen was conducted at room temperature after the preliminary oxidative and reductive treatment of samples at 550°C. A mixture of 10% H₂ + Ar was injected as pulses into a flow of argon at regular time intervals. A detector measured the amount of the adsorbate that did not react with the active metal. The injection continued until a constant TCD signal. The dispersion of the metal (D_{H_2}) was calculated as a ratio of the quantity of surface platinum atoms measured by the chemisorption of hydrogen to their total quantity with consideration for the H : Pt = 1 : 1 stoichiometry of sorption.

The dehydrogenation of propane was performed in a fixed-bed flow reactor with a catalyst (sample

tion of each experiment was 5 h. The composition of products was determined on-line on a Tsvet 500 gas chromatograph (Russia) equipped with a Pt-Alumina PLOT column (Restek, United States) with a length of 50 m and a flame-ionization detector.

n-Decane was dehydrogenated in an isothermal flow reactor (catalyst weight, 0.50 g) at a temperature of 460°C, a pressure of 0.18 MPa, an H_2/n -decane molar ratio of 7, and a weight hour space velocity of 17.2 h⁻¹. The catalysts were preliminarily calcined in air at 550°C and reduced in a flow of hydrogen at 400°C. The composition of products was analyzed in the on-line mode by taking samples from the reaction zone and supplying them to a Tsvet 800 gas chromatograph (Russia) equipped with a PONA/PIONA column (J & W Scientific, United States) and a flame-ionization detector. In the course of *n*-decane conversion, the group composition of the products was monitored: C_1-C_8 alkanes (cracking products), isodecanes (*iso*- C_{10}), *n*-decenes (C_{10} olefins), and diolefins $(C_{10} \text{ dienes})$. The formation of aromatic hydrocarbons under the reaction conditions was not observed.

RESULTS AND DISCUSSION

Characteristics of the Supports

For the preparation of platinum catalysts, MgAl-LDH with the ratios Mg/Al = 2, 3, and 4 were synthesized. According to X-ray diffraction data, all of the samples had an LDH structure. A characteristic set of reflections was present in the diffraction patterns [17]: a series of basal reflections 003 and 006 and the peaks of the families {0kl} (012, 015, 018) and {hk0} (110 and 113) (no. 22-700, ICDD, PDF-2) (Fig. 1, curve *I*).

Note that this hydrotalcite-like structure remained upon changes in the composition of interlayer anions in the course of catalyst synthesis (Fig. 1, curves 2-4). Thus, the analysis of the structural parameters of LDHs (as an example, structural data for the ratio Mg/Al = 2 are given) showed that the parameter c somewhat decreased (from 22.77 to 22.68 Å) on the formation of the "activated" form of LDH in the process of oxide phase rehydration and, correspondingly, upon the partial replacement of interlayer carbonate anions by hydroxide ones. However, the subsequent anion exchange that occurred on the interaction of MgAl-LDH-OH with the chloro complexes of Pt(II) and Pt(IV) led to an increase in the distance between the layers, which confirms the preferred localization of complexes in the interlayer space. Because the effect of the adsorption of the chloro complexes of platinum on the structural parameters in the synthesis



Fig. 1. Diffraction patterns of (1) MgAl-LDH-CO₃, (2) MgAl-LDH-OH, (3) [PtCl₆]²⁻/MgAl-LDH-OH, and (4) [PtCl₄]²⁻/MgAl-LDH-OH. The Mg/Al ratio is 2; the Pt content is 3 wt %.

of low-percentage catalysts is insignificant, Fig. 1 shows the diffraction patterns of samples with higher platinum content to illustrate the effect of intercalation. Upon the adsorption of $[PtCl_6]^{2-}$ or $[PtCl_4]^{2-}$, the parameter *c* increased from 22.68 to 22.98 or 23.11 Å, respectively. At the same time, the sequence of anion exchanges $CO_3^{2-} \rightarrow OH^- \rightarrow [PtCl_6]^{2-}$ ($[PtCl_4]^{2-}$) did not cause a substantial change in the cationic composition of hydroxide layers, and the parameter *a* retained its value (3.045–3.050 Å) even upon interaction with a sufficiently concentrated solution of $H_2[PtCl_6]$, when a significant amount of platinum (12 wt %) was introduced.

An increase in the Mg/Al ratio leads to an increase in the lattice parameter a as a result of a decrease in the fraction of aluminum cations, which possess a smaller ionic radius, and to an increase in the parameter cbecause of a decrease in the positive charge of hydroxide layers and in the interacting force between the layers and the interlayer anions (Table 1) [18].

The decrease of the positive charge of hydroxide layers upon a decrease in the fraction of triply-charged aluminum cations and, because of this, in the quantity of charge-compensating interlayer anions and the

Table 1. Structural characteristics of the MgAl-LDH samples and the textural characteristics of MgAlO_x

Mg/Al	MgAl	-LDH	MgAlO _x			
	<i>a</i> , Å	c, Å	S _{BET} , m²/g	$V_{\text{pore}},$ cm ³ /g	pore size, Å	
2	3.044	22.77	241	1.09	181	
3	3.064	23.46	202	0.81	161	
4	3.074	23.77	119	0.44	148	

strength of their interaction with the aluminum—magnesium hydroxide layers was accompanied by a monotonic decrease in the specific surface area and the pore volume and the average pore size in the resulting oxide phases with an increasing Mg/Al ratio (Table 1).

Anchoring of the Anionic Complexes of Platinum

Anchoring of the chloro complexes of Pt(II) and Pt(IV). The chloro complexes of platinum were adsorbed from the aqueous solutions of $H_2[PtCl_6]$ and $H_2[PtCl_4]$ onto MgAl-LDH in an "activated" form. The influence of the Mg/Al ratio on this process was studied by analyzing the adsorption isotherms of the corresponding complexes. The Mg/Al ratio in the MgAl-LDH samples was 2, 3, or 4 (Fig. 2).

An analysis of the adsorption isotherms of [PtCl₆]²⁻ complexes on MgAl-LDH showed that the adsorption (quantity) of immobilized complexes monotonically decreased with the Mg/Al ratio (Fig. 2a). This is consistent with the previously observed decrease in the positive charge of layers and a corresponding decrease in the number of charge-compensating interlayer anions [19]. The maximum adsorption varied from 0.75 to 1.06 mmol/g, which corresponds to 16-20 wt % adsorbed platinum. The stoichiometric amounts of the interlayer anions [PtCl₆]²⁻ calculated from a general formula for LDHs [17] with the assumption of the immobilization of platinum in the interlayer space as a result of the exchange of the complex anions with the interlayer ions OH⁻ in the samples with the ratios Mg/Al = 2, 3, and 4 were 1.45, 1.30, and 1.17 by mmol/g, respectively. These values are close to the experimental data. It is likely that the experimental values are somewhat lower due to the

presence of an amount of the interlayer ions CO_3^{2-} , which are incorporated, as a rule, in the course of experiments performed in an atmosphere of air.

Unlike the adsorption of [PtCl₆]²⁻, inverse dependence was observed on the immobilization of $[PtCl_4]^{2-}$ on MgAl-LDH samples with different Mg/Al ratios: the amount of anchored complexes increased with the Mg/Al ratio (Fig. 2b). The adsorption capacity of the supports with Mg/Al = 2 and 3 was 0.91-1.14 mmol/g (16-18 wt % Pt). At Mg/Al = 4, the amount of adsorbed complexes reached a maximum value of 1.37 mmol/g (22 wt % Pt), which exceeds the calculated amount of complex anions to be adsorbed by anion exchange. An excess amount of adsorbed Pt(II) complexes upon intercalation, as compared with their stoichiometric amount, allowed us to assume that a portion of platinum was unchored by another mechanism. It is likely that, because of a considerably higher lability of the chloro complexes of Pt(II) in comparison with that of Pt(IV) complexes [20], the former undergo rapid hydrolysis with the formation of platinum oxide species on the surface of a basic support. As



Fig. 2. Isotherms of the adsorption of (a) $[PtCl_6]^{2-}$ and (b) $[PtCl_4]^{2-}$ complexes on the MgAl-LDH samples with Mg/Al ratios of (1) 2, (2) 3, and (3) 4.



Fig. 3. (a) DRES of the chloro complexes of platinum supported onto MgAl-LDH: (1) $[PtCl_6]^{2-}$ (sample with Mg/Al = 3), (2) $[PtCl_6]^{2-}$ (sample with Mg/Al = 4), (3) $[PtCl_4]^{2-}$ (sample with Mg/Al = 3), and (4) $[PtCl_4]^{2-}$ (sample with Mg/Al = 4); (b) DRES of the carbonyl complexes of platinum supported onto MgAlO_x: (1) Mg/Al = 3 and (2) Mg/Al = 4.

the support basicity was increased, the amount of the hydrolyzed forms of platinum increased with the Mg/Al ratio, and this was accompanied by an increase in the amount of immobilized platinum and by a color change from pink to brown in the adsorbed precursors. This assumption is consistent with the results of a DRES study of the composition of immobilized complexes (Fig. 3).

According to published data [21], the nonhydrolyzed complexes [PtCl₆]²⁻ are characterized by absorption bands at 21000, 27000 (forbidden d-dtransitions in the central atom) and 38000 cm⁻¹ (charge transfer between the metal and the ligands).

KINETICS AND CATALYSIS Vol. 58 No. 4 2017

These bands were detected in the DRES spectra of the $[PtCl_6]^{2-}/MgAl-LDH$ supported systems (Fig. 3a, spectra *I* and *2*) regardless of the Mg and Al content of the support. The intensity ratios of these absorption bands were almost identical in the spectra of the systems with different Mg/Al ratios. Consequently, on the adsorption of the inert complexes $[PtCl_6]^{2-}$ on MgAl-LDH, they did not undergo considerable hydrolysis.

At the same time, on the adsorption of the chloro complexes of Pt(II), the composition of the adsorbed complexes changed with the Mg/Al ratio (Fig. 3a, spectra 3 and 4). At Mg/Al = 3, the surface complexes



Fig. 4. ¹⁹⁵Pt NMR spectra of (1) the chloro complexes of platinum in solution and (2) the above complexes supported onto MgAl-LDH-OH: (a) $[PtCl_6]^{2-}$ and (b) $[PtCl_4]^{2-}$. The Mg/Al ratio was 2; the platinum content was 15 wt %.

had the formula $[Pt(H_2O)Cl_3]^-$ and exhibited characteristic absorption bands at 42000, 30800, and 25700 cm⁻¹ [22], whereas the fraction of more deeply hydrolyzed forms increased at Mg/Al = 4. This manifested itself in a shift of the "ligand" \rightarrow metal charge transfer band (42000 cm⁻¹) to the region of higher wavenumbers with a decrease in its intensity. In this case, the bands at 25600 and 31300 cm⁻¹ were strongly smeared.

The ¹⁹⁵Pt NMR-spectroscopic study of the $[PtCl_6]^{2-}/MgAl-LDH$ sample also demonstrated the presence of nonhydrolyzed complex species. Spectrum 2 in Fig. 4a exhibits only one signal with a chemical shift of about 70 ppm, which corresponds to $[PtCl_6]^{2-}$. Other signals were not detected over a wide range. Furthermore, ¹⁹⁵Pt MAS NMR spectroscopy provides information on the interactions of metal complexes with the surface. It is well known that the signals of supported [PtCl₆]²⁻ complexes in the ¹⁹⁵Pt NMR spectra are observed only in the case that their octahedral symmetry remains unchanged or becomes weakly distorted upon adsorption (for example, as a result of electrostatic interaction) [23]. NMR signals were absent upon more specific adsorption on the support. Because the NMR spectrum exhibited the signals of the adsorbed chloro complexes of platinum with chemical shifts in a region close to the region of their absorption in solution (Fig. 4a, spectrum 1), we assumed that the anchoring of the chloro complexes of Pt(IV) onto MgAl-LDH did not cause a distortion in the symmetry of metal complex polyhedrons and it was caused by Coulomb interaction between positively charged aluminum-magnesium hydroxide layers and negatively charged chloroplatinate ions.

Fundamentally different results were obtained in the ¹⁹⁵Pt MAS NMR-spectroscopic study of the adsorption

of the chloro complexes of Pt(II). The spectrum of $[PtCl_4]^{2-}$ complexes in aqueous solution exhibited a chemical shift at -1600 ppm (Fig. 4b, spectrum *I*). The NMR signals were absent from the spectra of the $[PtCl_4]^{2-}$ /MgAl-LDH samples regardless of the Mg/Al ratio (Fig. 4b, spectrum *2*). It is likely that this system is characterized by other metal complex–support interactions. In the case of the intercalation of the square-planar complexes of Pt(II) into the interlayer space, they can be additionally coordinated to the OH⁻ groups of the hydroxide layers of MgAl-LDH. The symmetry of complexes also changed upon the immobilization of platinum oxide species, which occur on the surface of the most basic supports.

Anchoring of the carbonyl complexes of Pt(0). The carbonyl complexes of platinum $[Pt_3(CO)_6]_6^{2-}$ were adsorbed from an acetone solution on the mixed oxides MgAlO_x (MgAl-LDHs calcined at 550°C) under the conditions that prevented the penetration of air into the system (to prevent the premature destruction of the complexes). Their adsorption was rapid and complete, and it was accompanied by the discoloration of the initial olive-green solution. In this case, the support acquired a garnet red nuance caused by the presence of the lower nuclearity complexes $[Pt_3(CO)_6]_3^{2-}$ with a characteristic color on the support surface [24]. This chemical composition of the immobilized complexes was confirmed by the results of the DRES study (Fig. 3b). Absorption bands at 17800, 20000, and 27600 cm^{-1} , with are characteristic of the $[Pt_3(CO)_6]_3^{2-}$ complexes in solution [24], were present in the electron spectra. The absence of pronounced bands due to the carbonyl complexes of another composition is indicative of the high uniformity of an adsorption coating.

Mg/Al	Pt, wt %	Precursor	Conversion, %	Selectivity, %	DI*, %	$D_{\mathrm{H2}},\%$
2	0.24		12.2	98.4	48	44
3	0.23	$H_2[PtCl_6]$	7.7	98.0	55	33
4	0.21		4.4	97.9	64	21
2	0.17	H ₂ [PtCl ₄]	14.8	97.0	46	58
3	0.20		11.6	97.4	47	32
4	0.17		6.6	98.2	59	18
2	0.21		19.6	95.5	23	95
3	0.22	$[Pt_3(CO)_6]_6^{2-}$	20.4	92.9	25	91
4	0.21		21.3	92.5	28	90

Table 2. Results of the catalytic tests of $Pt/MgAlO_x$ samples in the dehydrogenation of propane

* Deactivation index $DI = 100(X_{initial} - X_{final})/X_{initial}$, where $X_{initial}$ and X_{final} are the propane conversions after catalyst operation for 10 min and 5 h, respectively.

The use of mixed oxides and acetone solutions for the supporting of carbonyl complexes made possible the immobilization of metal complexes directly on the support surface without the restoration of the laminar structure of LDHs (which occurs on the adsorption of complexes on the mixed oxides from aqueous solutions [19]). This approach ensured the minimum degree of metal complex-support interactions, and the size of the supported particles of platinum was determined by only the complex nuclearity and the porous structure of the oxide support. Unlike the adsorption of the chloro complexes of platinum, the variation of the basicity of the oxide support MgAlO_x does not exert a substantial effect on the composition of the immobilized carbonyl complexes, which was almost identical in all of the $[Pt_3(CO)_6]_6^{2^-}/MgAlO_x$

almost identical in all of the $[Pt_3(CO)_6]_6^-$ /MgAIO_x supported systems regardless of the Mg/Al ratio, according to the DRES data.

Catalytic Properties of the Samples

Catalytic properties of the samples in the dehydrogenation of propane. The samples with different Mg/Al ratios (2, 3, and 4) were prepared with the use of platinum precursors of different composition (the chloro complexes of Pt(IV) and Pt(II) and the carbonyl complexes of platinum) for studying the catalytic properties of the Pt/MgAlO_x systems in the dehydrogenation reaction of propane. The calculated platinum content of the catalysts was 0.2 wt %. Table 2 summarizes the results of catalytic tests, specifying the real Pt content and dispersion.

In the samples obtained from the chloride precursors of platinum, a correlation between their catalytic activity and the composition of a support was observed. The less dispersed particles of platinum were formed upon the anchoring of the chloro complexes of Pt(II) and Pt(IV) predominantly in the interlayer space of LDHs, which was accompanied by a decrease in the positive charge of layers (with a decrease in the fraction of trivalent cations) and by the corresponding weakening of the strength of the interaction of anionic complexes with the support. This led to a monotonic decrease in the catalyst activity with increasing the Mg/Al ratio. The higher activity of the samples based on $[PtCl_4]^{2-}$ can be a consequence of the increased dispersion of the portion of platinum formed from the intercalated complexes. The possibility of the additional coordination of square-planar complexes decreases their mobility in the interlayer space and the probability of the formation of larger platinum particles in the course of heat treatment. This effect was most distinctly pronounced in the case of the sample obtained with the use of the least basic support (Mg/Al = 2), in which the fraction of platinum particles formed from the hydrolyzed forms of Pt(II) complexes was minimal.

In the catalysts prepared with the use of the carbonyl complexes of platinum, the dispersion of platinum was the highest (90-95%), and the degree of propane conversion on them, which weakly depends on the Mg/Al ratio, reached a maximum.

Note that the target product was formed with high selectivity on the samples in which strong interaction between platinum and a basic support occurred on the intercalation of a metal complex precursor. The relatively lower selectivity for the formation of propylene on the samples prepared by the decomposition of carbonyl complexes on the surface of a mixed oxide and their lowered deactivation was caused by their increased cracking ability (Fig. 5).

Catalytic properties of the samples in the dehydrogenation of *n*-decane. The effect of the composition of an active component precursor on the properties of Pt/MgAlO_x catalysts was also studied in the dehydrogenation reaction of *n*-decane. In the conversion pro-



Fig. 5. Time dependence of the yield of C_1-C_2 cracking products (methane, ethane, and ethylene) on the Pt/MgAlO_x catalysts prepared with the use of different active component precursors: (1) [PtCl₆]²⁻, (2) [PtCl₄]²⁻, and (3) [Pt₃(CO)₆]₆²⁻. The Mg/Al ratio was 2.

cesses of higher alkanes, the contribution of side reactions is important; therefore, higher requirements are imposed on the platinum centers responsible for the occurrence of the target reaction than those in the dehydrogenation of light alkanes. Table 3 and Fig. 6 summarize the results of studying the samples with a 0.2% Pt content, which were synthesized from the chloro complexes of Pt(II) and Pt(IV) and the carbonyl complexes of Pt(0).

As in the dehydrogenation of propane, the catalyst prepared from the carbonyl complexes exhibited a maximum activity; however, the selectivity of the formation of alkenes on it was comparatively low. In spite of its high basicity (because of the use of a chloride-free precursor), side reactions occurred to a considerable degree on the surface of this sample. As compared with the catalysts prepared from the complexes $[PtCl_6]^{2-}$ and $[PtCl_4]^{2-}$, it possessed noticeable isomerizing and cracking activity. Thus, the amounts of cracking products and dienes formed on it were greater by factors of 13 and 5, respectively, as compared with those formed on the catalysts synthesized the use of the chloro complexes of Pt(IV) and Pt(II) (Fig. 6).



Fig. 6. Dependence of the yield of *n*-decane dehydrogenation products on the composition of active component precursors after catalyst operation for 3 h: (1) $[PtCl_6]^{2-}$, (2) $[PtCl_4]^{2-}$, and (3) $[Pt_3(CO)_6]_6^{2-}$. The Mg/Al ratio was 2.

It is likely that the state of platinum produced with the use of intercalated chloro complexes is more preferable for the selective dehydrogenation of n-decane to n-decene. In this case, the strong metal—support interaction with electron density transfer from the basic support to platinum particles can manifest itself; as a result of this, the strength of the adsorption of reagents on platinum decreases to influence the reaction path of the conversion of n-decane molecules and the desorption of the reaction products.

CONCLUSIONS

Thus, in this work, we found that the selection of an active component precursor makes it possible to regulate the properties of Pt/MgAlO_x catalysts in the dehydrogenation reactions of propane and *n*-decane. Catalysts with different dispersions of supported platinum were prepared by the anchoring of various complex compounds of platinum ([PtCl₆]²⁻, [PtCl₄]²⁻, and [Pt₃(CO)₆]₆²⁻) on layered aluminum–magnesium hydroxides and corresponding oxides with different Mg/Al ratios. The highly dispersed catalysts synthesized with the use of the carbonyl compounds of plat-

Table 3. Results of the catalytic tests of $Pt/MgAlO_x$ samples in the dehydrogenation reaction of *n*-decane (the ratio Mg/Al = 3)

Precursor	Pt content, wt %	<i>n</i> -Decane conversion, %	Selectivity, %	$D_{\mathrm{H2}},\%$
H ₂ [PtCl ₆]	0.19	5.5	94.0	26
H ₂ [PtCl ₄]	0.19	6.2	93.5	32
$[Pt_3(CO)_6]_6^{2-}$	0.18	7.9	62.0	91

2017

No. 4

KINETICS AND CATALYSIS Vol. 58

EFFECT OF THE NATURE OF THE ACTIVE-COMPONENT PRECURSOR

inum exhibited the greatest activity in alkane conversion processes. At the same time, in contrast to a reaction with the participation of propane, the state of platinum acquired upon the intercalation of the chloro complexes of platinum into the interlayer space of LDHs is optimal for the selective formation of target alkenes from higher alkanes.

Thus, the catalytic system $Pt/MgAlO_x$ is capable of ensuring high selectivity for the formation of alkenes in the dehydrogenation of light and higher alkanes. Further research to be performed under the conditions that ensure an increase in the conversion of reagents (an increase in the reaction temperature and a smaller dilution with hydrogen) with studying the stability and regenerability of the catalysts will make it possible to compare the currently available platinum catalysts for dehydrogenation [25] with the samples based on LDHs examined in this work and to evaluate prospects for the application of these latter to industrial dehydrogenation processes.

ACKNOWLEDGMENTS

This study was carried out in the framework of research work no. 17120V of Omsk State Technical University using equipment of the Omsk Shared Facilities, Siberian Branch, Russian Academy of Sciences.

REFERENCES

- 1. Li, X., Kant, A., He, Y., Thakkar, H.V., Atanga, M.A., Rezaei, F., Ludlow, D.K., and Rownaghi, A.A., *Catal. Today*, 2016, vol. 276, p. 62.
- Akporiaye, D., Jensen, S.F., Olsbye, U., Rohr, F., Rytter, E., Rønnekleiv, M., and Spjelkavik, A.I., *Ind. Eng. Chem. Res.*, 2001, vol. 40, p. 4741.
- Ballarini, A.D., Miguel, S.R., Castro, A.A., and Scelza, O.A., *Appl. Catal.*, *A*, 2013, vol. 467, p. 235.
- Sheintuch, M., Liron, O., Ricca, A., and Palma, V., *Appl. Catal.*, *A*, 2016, vol. 516, p. 17.
- Xia, K., Lang, W.-Z., Li, P.-P., Yan, X., and Guo, Y.-J., J. Catal., 2016, vol. 338, p. 104.
- Volynkin, A., Ronning, M., and Blekkan, E.A., *Top. Catal.*, 2015, vol. 58, p. 854.
- Zhu, H., Anjum, D.H., Wang, Q., Abou-Hamad, E., Emsley, L., Dong, H., Laveille, P., Li, L., Samal, A.K., and Basset, J.-M., *J. Catal.*, 2014, vol. 320, p. 52.

- Sha, L., Nan, W., Bo, Z., Song-bo, H., Jie-shan, Q., and Cheng-lin, S., *J. Fuel Chem. Technol.*, 2013, vol. 41, no. 12, p. 1481.
- 9. Voronetskii, V.S., Didenko, L.P., and Savchenko, V.I., *Khim. Fiz.*, 2009, vol. 28, no. 4, p. 48.
- 10. Cosimo, J.I.D., Diez, V.K., Xu, M., Iglesia, E., and Apesteguia, C.R., *J. Catal.*, 1998, vol. 178, p. 499.
- 11. Wang, Q. and O'Hare, D., *Chem. Rev.*, 2012, vol. 112, p. 4124.
- Wang, J., Wang, L., Chen, X., Lu, Y., and Yang, W., J. Solid State Electrochem., 2015, vol. 19, no. 7, p. 1933.
- 13. Mascolo, G. and Mascolo, M.C., *Microporous Mesoporous Mater.*, 2015, vol. 214, p. 246.
- 14. *Handbuch der preparativen anorganischen Chemie*, von Brauer, G., Ed., Stuttgart: Ferdinand Enke, 1981.
- Matveev, K.I., Rachkovskaya, L.N., and Eremenko, N.K., *Izv. Sib. Otd. Akad. Nauk SSSR*, 1968, no. 2, p. 81.
- Bel'skaya, O.B., Leont'eva, N.N., Gulyaeva, T.I., Drozdov, V.A., Doronin, V.P., Zaikovskii, V.I., and Likholobov, V.A., *Kinet. Catal.*, 2011, vol. 52, no. 6, p. 761.
- 17. Cavani, F., Trifiro, F., and Vaccary, A., *Catal. Today*, 1991, vol. 11, p. 173.
- Leont'eva, N.N., Cherepanova, S.V., Belskaya, O.B., Drozdov, V.A., and Talzi, V.P., *Chem. Sustainable Dev.*, 2013, vol. 21, no. 1, p. 61.
- Bel'skaya, O.B., Gulyaeva, T.I., Leont'eva, N.N., Zaikovskii, V.I., Larina, T.V., Kireeva, T.V., Doronin, V.P., and Likholobov, V.A., *Kinet. Catal.*, 2011, vol. 52, no. 6, p. 876.
- Pishchevitskii, B.I., Belyaev, A.V., Shchekochikhina, R.L., and Mal'chikov, G.D., *Kinetika reaktsii zameshcheniya ligandov* (Kinetics of Ligand Substitution Reactions), Novosibirsk: Nauka, 1974.
- 21. Buslaeva, T.M., Umreiko, D.S., Novitskii, G.G., Sinitsyn, N.M., and Kovrikov, A.B., *Khimiya i spektroskopiya galogenidov platinovykh metallov* (Chemistry and Spectroscopy of Platinum Metal Halides), Minsk: Universitetskoe, 1990.
- 22. Zolotov, Yu.A., Varshal, G.M., and Ivanov, V.M., in *Analiticheskaya khimiya metallov platinovoi gruppy* (Analytical Chemistry of Platinum-Group Metals), Moscow: Editorial URSS, 2003, p. 592.
- 23. Shelimov, B.N., Lambert, J.-F., Che, M., and Didillon, B., J. Mol. Catal. A: Chem., 2000, vol. 158, p. 91.
- 24. Longoni, G. and Chini, P., J. Am. Chem. Soc., 1976, vol. 98.

Translated by V. Makhlyarchuk