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Zinc influence on the formation and properties of Pt/Mg(Zn)AlO$_x$ catalysts synthesized from layered hydroxides

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ABSTRACT

Layered double hydroxides (LDH) containing Al^{3+}, Mg^{2+} and Zn^{2+} cations with the ratios of Zn/(Mg + Zn) = 0, 0.05, 0.1, 0.2, 0.5, 0.7, and 1.0 were synthesized. The effect of zinc content on the phase composition of LDH and on the structural parameters, textural characteristics and acid–base properties of the corresponding mixed oxides were studied. This type of supports was used to obtain the non-acid platinum Pt/Mg(Zn)AlO$_x$ catalysts. The formation of supported platinum particles, their composition, dispersion and electronic state were examined by means of TPR, TEM, XPS, and EXAFS. The possibility to obtain the bimetallic PtZn particles, whose structure and strength of interaction with the support depend on the zinc content of the support, was demonstrated. It was found that the presence of zinc atoms in the platinum environment decreases the particle size of active metal and stabilizes platinum in the active metallic state ensuring a high activity of the catalyst in dehydrogenation of propane with the selectivity for propylene above 99%.

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1. Introduction

Layered double hydroxides (LDH) with the general formula [M(II)$_{1-x}M$(III)$_x$(OH)$_2$][A^{n-}]$_{x/n}$ mH$_2$O, where M is a metal and A is an anion, are widely employed in various fields [1–6]. The catalytic application of these materials is related to the synthesis of multicomponent catalysts for aldol condensation, alkylation, polymerization, hydrogenation, steam reforming and other reactions [7–10]. The main advantages of LDH as catalyst precursors list the possibility to use various cationic pairs in the formation of a layered structure and hence the synthesis of materials with different controllable properties; the distribution of cations in the LDH structure at the atomic level, which prevents their significant segregation during further treatments; and the formation of mixed oxides with a developed surface area upon decomposition of LDH. The application of mixed oxides produced by thermal treatment of magnesium–aluminum LDH as non-acid supports for platinum catalysts ensures the high stability of the catalysts under the coking conditions and during the redox treatment [11,12]. Thus, one of the promising applications of such catalysts is the high-temperature dehydrogenation of alkanes [13–21]. Particular attention is drawn to the supports containing LDH, where aluminum or magnesium cations are partially substituted by other elements that are able not only to affect the characteristics of support (textural parameters and acid–base properties) but also to modify the properties of platinum [18–21].

Modification of the catalytic behavior of a noble metal by adding the second inactive metal that can form an alloy or intermetallic compound is a topical field in heterogeneous catalysis [22–28]. The brightest example is the platinum–tin system supported on alumina. This composite has been widely used in gasoline reforming and dehydrogenation of alkanes, demonstrating higher activity and stability as compared with monometallic platinum catalyst [22–28]. The mechanism of the promoting action of tin was studied in detail. Tin and platinum are supposed to form bimetallic alloys

of different composition, which ensure the dissociative adsorption of alkanes and diminish the adsorption of alkenes as the target products. Platinum–tin catalysts can be synthesized also with SiO_2, zeolites [29,30] and stoichiometric spinels [31–33] as the supports; such catalysts are employed in dehydrogenation of light alkanes, oxidation of CO, and selective hydrogenation of the carbonyl group in unsaturated aldehydes [34–39]. Platinum–tin composites supported on mixed oxides made from magnesium–aluminum LDH are also known. In this case, the step of anchoring the active component, which excludes structural transformations of the oxide support, is quite complicated. It consists in the deposition of either a colloidal suspension of bimetallic PtSn particles or acetylacetonate complexes of platinum and tetra *n*-butyl tin in organic solvents in the absence of air [16,17]. A more promising method of adding a modifier is its introduction in the oxide support precursor, LDH. Thus, in some works [18–21], the properties of platinum were modified by introducing indium and gallium cations into MgAl-LDH during coprecipitation of hydroxides.

The purpose of the present work was to synthesize the LDH containing aluminum, magnesium and zinc cations upon variation of the zinc fraction in the composition of bivalent components, and to elucidate the effect of zinc content on the properties of oxide supports and supported platinum. Dehydrogenation of propane served as a model reaction for estimating the effect of the composition of support on the dehydrogenating activity of platinum.

The effect of the features of a bivalent metal on the structural and textural characteristics of LDH and the corresponding mixed oxides was studied in our earlier work [40]. It was shown that the structure and properties of zinc-containing LDH are close to those of magnesium–aluminum system, and these LDH can form the oxide phase with a developed surface area. The use of zinc for modification of platinum properties is well known [22,41–43]. The platinum–zinc system resembles the platinum–tin one. Platinum and zinc also can form alloys of different stoichiometry (for example, PtZn and Pt_3Zn), which differ from monometallic platinum catalysts in the catalytic properties. In addition, zinc oxide is the *n*-type semiconductor, and its strong interaction with platinum is quite expectable. Therefore, platinum catalysts with ZnO as the support are being studied intensively [44–48].

The improvement of catalytic characteristics in hydrogenation and dehydrogenation reactions is commonly attributed to the formation of a Pt–Zn alloy upon reduction of Zn(II) in the presence of platinum [22,44]. It is believed that the interaction between these metals and changes in the electronic state of platinum weakens the Pt–(C–C) bond, thus facilitating the desorption of olefins [49]. A further investigation of the adsorption of ethylene and formaldehyde on Pt, Pt_3Zn and PtZn [49] confirmed a weaker adsorption of olefins and carbonyl compounds on bimetallic particles. One of the approaches to revealing the nature of platinum–zinc interaction is the deposition of these metals on a relatively inert carbon support [22,50,51]. Thus, the formation of bimetallic PtZn particles was observed in the catalyst that showed a high activity in the dehydrogenation of isobutane with 100% selectivity for isobutylene [25]. Pt–Zn/C catalysts also showed a much higher activity and stability in the oxidation of BH_4 as compared with Pt/C. A study with variation of the zinc content demonstrated that a catalyst of the composition $Pt_{67}Zn_{33}$/C had the maximum activity [50]. The effect of zinc on the properties of platinum catalysts already containing tin as a promoter was reported [52,53]. The introduction of zinc into Pt–Sn/ZSM-5 increased the selectivity for propylene in propane dehydrogenation [52]. Zn addition to the PtSnK/γ-Al_2O_3 catalyst not only increased the platinum dispersion but also decreased coking of the surface in the dehydrogenation of isobutane. The authors of [56] suggest that the presence of zinc enhances the interaction of tin with the support and inhibits the process of tin reduction.

It should be noted that, unlike in the works [16–21,54–56] where platinum was anchored by impregnation of the calcined LDH with toluene solutions of acetylacetonate platinum, in this study the maximum interaction of platinum with the modifying cation was provided by platinum anchoring via intercalation of Pt(IV) anionic chloride complexes into the interlayer space of zinc-containing LDH. This anchoring method made it possible to use aqueous solutions of the metal complex. The authors of [57–59] tried to anchor the active metal via its interaction with a hydroxide precursor of the support. In [57], platinum was introduced as $Pt(acac)_3$ or $H_2Pt(OH)_6$ during the synthesis of ZnAl-LDH by the sol–gel method. However, this did not provide the anchoring of platinum from the acetylacetonate precursor; the introduction of $H_2Pt(OH)_6$ did not produce any changes in the structural parameters and gave no grounds to make a conclusion on platinum localization. In [58,59], intercalation of metal complexes was performed under hydrothermal conditions, which led to significant changes in the chemical composition of the complexes.

In this work, anionic platinum complexes were anchored using the activated LDH species (LDH-OH) whose interlayer space was filled mostly with the charge compensating OH^- anions. These anions possess better exchange properties than carbonate anions intercalating into the interlayer space directly during the LDH synthesis [14,60]. Upon interaction of chloroplatinate with LDH-OH, the interlayer OH^- ions are readily substituted by the doubly charged complex anions $[PtCl_6]^{2-}$. An additional driving force of this process is the neutralization of interlayer OH^- anions by hydrogen ions of chloroplatinic acid. In this case, chloroplatinate is anchored via electrostatic interaction with the positively charged LDH layers without noticeable changes in the composition and symmetry of the complex [14].

2. Experimental

2.1. Catalyst preparation

The synthesis of the layered hydroxides having different composition and carbonate counter ions was described in detail in [1–5,13–15,40]. The synthesis procedure included coprecipitation of Mg^{2+}, Zn^{2+} and Al^{3+} hydroxides from aqueous solutions (1 mol/L) of nitrate salts upon their interaction with the solutions containing carbonate and hydroxide ions (1 mol/L). The molar ratio of cations $(Mg^{2+} + Zn^{2+})/Al^{3+}$ in the salt solution was maintained constant and equal to 2. The variable fraction of zinc ions in the composition of bivalent cations $Zn^{2+}/(Mg^{2+} + Zn^{2+})$ was 0, 0.05, 0.1, 0.2, 0.5, 0.7, 1.0. These values were then used to denote the synthesized samples. The synthesis was carried out at pH = 10 and a temperature of 333 K. The resulting precipitates of layered hydroxides with interlayer carbonate anions $Mg(Zn)Al-CO_3$ were washed and dried for 16 h at 353 K. To obtain samples of activated LDH, i.e. those containing mostly the interlayer OH^- anions (Mg(Zn)Al-OH), the initial ($Mg(Zn)Al-CO_3$) support was calcined at 823 K and hydrated once more in distilled degassed water. The calcination temperature was chosen from thermal analysis data and corresponded to a complete formation of the oxide phase. The hydration of mixed oxide led to restoration of the LDH layered structure (the memory effect) with appropriate changes in the composition of the interlayer space [13–15].

Chloroplatinic acid (Aurat Ltd., Specs. 6-09-2026-87) was adsorbed from an excess of aqueous solutions on the Mg(Zn)Al-OH support via the exchange of interlayer OH^- anions with $[PtCl_6]^{2-}$ anions [14,60]. Prior to physicochemical examination, hydroxide precursors of the supports were calcined at 823 K, and LDH with the deposited complexes ($Mg(Zn)Al-PtCl_6$) were calcined