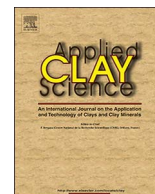




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Research paper

SEM study of the surface morphology and chemical composition of the MgAl- and MgGa-layered hydroxides in different steps of platinum catalysts Pt/Mg(Al, Ga)O_x synthesis

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ABSTRACT

The surface morphology and chemical composition of the MgAl- and MgGa-layered hydroxides as supports precursors were studied by SEM and EDX in all steps of the platinum catalysts Pt/Mg(Ga, Al)O_x synthesis. The study revealed a higher structural stability of Ga-containing samples in comparison with Al-containing analogs, which shows up as their morphological invariability during calcination, activation of layered double hydroxides, and anchoring of the metal complex. A similar Mg/M³⁺ ratio of metals estimated by both the volumetric method and EDX confirms that a uniform distribution of metals in the support is retained during the catalyst synthesis; this will ensure the specified adsorption and acid-base properties of Pt/MgAlO_x and Pt/MgGaO_x, which are the promising catalytic systems for dehydrogenation of light and higher alkanes.

1. Introduction

Layered double hydroxides (LDH), or hydrotalcites, are a class of inorganic compounds that have been studied intensively for several decades (Daud et al., 2016; Li et al., 2015; Rives et al., 2014; Theiss et al., 2016; Zümreoglu-Karan and Ay, 2012). LDH are the layered compounds with a general formula [M_{1-x}²⁺M_x³⁺(OH)₂](A^{m-})_x/m·nH₂O, where M²⁺ and M³⁺ are the cations of metals having different valences and close radii, $x = M^{3+}/(M^{2+} + M^{3+})$. Therewith, an excess positive charge of the hydroxide layers, which is formed due to the presence of different valence cations, is compensated by hydrated A^{m-} anions filling the interlayer space (Evans and Slade, 2006). Hydrotalcites are widely employed as adsorbents, anion exchangers, and catalysts of organic reactions requiring the presence of basic sites; their structural, textural, acid-base and anion-exchange properties are determined to a great extent by the nature and ratio of metals in the layers as well as by the amount and size of anions in the interlayer space (Fan et al., 2014). The moderate basicity and the possibility of its deliberate control by varying the cationic and anionic composition of LDH open up ample opportunities for their application as the precursors of supports for metal catalysts. Thus, a promising direction is the synthesis of platinum catalysts supported on the M₁M₂O_x mixed oxide, which is formed upon calcination of LDH at 500–650 °C, for dehydrogenation of alkanes

(Belskaya et al., 2016a, 2016b, 2015; Galvita et al., 2010; Siddiqi et al., 2010; Stepanova et al., 2016, 2013; Sun et al., 2010). The synthesis of such catalysts is a multistage process commonly comprising the following steps (Belskaya et al., 2016a, 2016b): synthesis of the initial LDH with the interlayer carbonate ions (LDH-CO₃); calcination of LDH-CO₃ to obtain the mixed oxide; rehydration of the mixed oxide with restoration of the layered structure to produce the “activated” LDH with the dominant content of hydroxyl anions in the interlayer space of (LDH-OH); introduction of the active component precursor in the interlayer space via the exchange of OH⁻ anions for [PtCl₆]²⁻; and thermal treatment of [PtCl₆]²⁻/LDH in the oxidizing and reducing atmosphere. The transformation of LDH-CO₃ to LDH-OH extends the synthesis process but is a necessary step because the optimized and reproducible synthesis of the carbonate form of LDH gives a material with low anion-exchange properties and weak basicity.

The surface morphology strongly determines the conditions of reagents adsorption and diffusion, and information on the surface layer composition allows estimating stability of the properties of the support upon its contact with a solution of the active component precursor and under high-temperature treatments. The morphology and chemical composition of the surface layer can be studied by scanning electron microscopy (SEM) using an appropriate set of attachments.

The morphology of LDH was examined by SEM in several works

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(Adelantado et al., 2003; Belskaya et al., 2011; Benito et al., 2006; Faour et al., 2010; Hibino and Ohya, 2009; Ma et al., 2008; Wang et al., 2012, 2011, 2010a, 2010b). The best studied systems are magnesium-aluminum ones (MgAl-LDH), the analogs of a natural mineral hydroxalite $\text{Mg}_6\text{Al}_2\text{CO}_3(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$. Q. Wang et al. (2012) investigated MgAl-LDH as adsorbents of CO_2 . The effect of various factors – cationic and anionic composition, methods and conditions of the synthesis – on the morphology of MgAl-LDH was studied. Conditions of the synthesis were found to be the key factor in the formation of the LDH structure. It was shown that LDH of different composition synthesized under similar conditions have the identical morphology. Since LDH are commonly synthesized by coprecipitation, the pH of the synthesis plays an important role and its value is usually equal or exceeds the pH of precipitation of the most soluble hydroxide. Therewith, different surface structures can be formed depending on the difference between the chosen pH of the synthesis and the point of zero charge (PZC, the pH value at which the total charge is zero) of the produced LDH. When these values are equal, LDH with the “rosette” morphology is formed. “Rosettes” are represented by platelets overlapping each other in different directions. If LDH are synthesized by coprecipitation, the formation of the primary particles is very fast, but their growth is slow due to electroneutrality of the surface at $\text{pH}_{\text{synth}} = \text{pH}_{\text{PZC}}$. As a result, the particle growth occurs mostly along the (001) plane, where the surface charge density is minimal, with the formation of the so-called “rosettes”. At a lower pH of the synthesis (6.5–9), the morphology of LDH is similar to that of $\gamma\text{-AlOOH}$, which is an aggregate of primary nanoparticles. At a high pH (above 14), when $\text{pH}_{\text{PZC}} < \text{pH}_{\text{synth}}$, the LDH particles are formed rapidly but their further growth does not occur. In the process, the particle surface has a negative charge, which weakens its interaction with $\text{Al}(\text{OH})^-$ or CO_3^{2-} in the solution. This results in the formation of a fine-grain material (Wang et al., 2012).

The synthesis of MgAl-LDH by the method based on carbamide decomposition also produced compounds with the rosette-like morphology. However, in distinction to hydroxalites obtained by coprecipitation, the authors of (Hibino and Ohya, 2009; Wang et al., 2010a) observed the formation of well crystallized hexagonal plate-shaped particles with a non-uniform particle size (~500 μm). These platelets of a few micrometer thickness were disordered and intermeshed with each other. The formation of such aggregates was attributed to the features of carbamide synthesis. At elevated pressure and temperature, NH_3 formed by decomposition of carbamide was supposed to interact with the hydroxyl groups of LDH layers. The evolved gas forms numerous small bubbles, which ultimately results in the aggregation of platelets in the gas-liquid interface. The proposed mechanism was verified by EDX data, according to which the obtained particles contain Mg, Al, O and N atoms. The synthesis of NiAl-LDH (Faour et al., 2010) by both the coprecipitation in a strongly alkaline medium and the decomposition of carbamide led to the formation of LDH with the rosette morphology (sand rose). Hydrothermal treatment of the produced LDH (except those synthesized with the use of carbamide) facilitated an increase in the particle size due to agglomeration of smaller particles as a result of partial dissolution–precipitation that occurred under hydrothermal conditions.

In some cases, the morphology of hydroxalites is affected not only by the synthesis conditions but also by the nature of cations and anions in the composition of LDH. According to (Siddiqi et al., 2010), in the case of MgAl- and MgGa-LDH, rosettes can associate into spheres. MgFe-LDH are characterized by the presence of flake-like particles with the size of 150–200 nm and ca. 25 nm thickness. The morphology of MgMn-LDH is represented by aggregates of nanoparticles with the size up to 35 nm (Wang et al., 2010b). Variation of interlayer anions showed that in a series of CO_3^{2-} , HCO_3^- , SO_4^{2-} , Cl^- only the carbonate-containing samples have the rosette morphology. The other samples have the stone-like morphology (Wang et al., 2011). It should be noted that the loose structure of rosettes promotes the formation of LDH- CO_2 porosity, whereas hydroxalites containing other anions do not have a

developed pore structure (Belskaya et al., 2011; Wang et al., 2011).

In addition to the rosette morphology, MgAl-LDH can have also the plate-like one. In this case, the particles in SEM images look like overlapping oval or hexagonal platelets. MgAl-LDH with such morphology can be produced with the use of carbamide under hydrothermal conditions at microwave radiation (Benito et al., 2006). The use of carbamide as a precipitating agent facilitates a slow formation of LDH particles since carbamide decomposes with the formation of a base only at a certain temperature. An exposure of the system to microwave radiation increases the rate of carbamide hydrolysis, thus promoting a faster formation of LDH with a large number of small crystals of a uniform size. The plate-like material was observed also for LDH of other cationic composition, for example, $\text{Co}^{2+}\text{Co}^{3+}$ -LDH (Ma et al., 2008). Although the unique morphology of LDH attracts considerable interest, SEM studies on the surface transformations of LDH-based supports during the catalyst synthesis are quite scarce. There are virtually no works where energy dispersive X-ray spectroscopy (EDX) was used for simultaneous analysis of changes in the surface chemical composition. However, EDX is employed for qualitative and quantitative analysis of the surface composition of metals and alloys (Adelantado et al., 2003; Suba et al., 1994; Winkler et al., 2007; Wu et al., 2012) as well as disperse materials, such as zeolites (Auroux et al., 1983; Majhi et al., 2015; Shoumkova and Stoyanova, 2013) and catalysts of various composition (Bednarova et al., 2002; Paksoy et al., 2015).

The goal of the work was to elucidate the effect of different processes (calcination, rehydration, and anionic exchange) in the synthesis of Pt/MgAlO_x and Pt/MgGaO_x catalysts on the morphology and chemical composition of the support surface layer by means of scanning electron microscopy and analytical potential of an energy dispersive spectrometer. Since a highly uniform distribution of components in the structure of the support material is considered as one of the most important characteristics of double hydroxides and the corresponding mixed oxides, this study was aimed to reveal whether this advantage is retained during multistep treatments. The selectivity of the target products formation and electronic state of the active component depend on the metals ratio in LDH. With increasing Mg/Al ratio the growth of LDH basic properties occurs, which promotes to reduce of the proportion of platinum is in an oxidized state. It is known that electron deficient platinum particles have the ability to adsorb olefins more strongly. This can cause of further dehydrogenation of that olefins and, consequently, to reduce catalysts selectivity through the formation of side products with greater number of carbon atoms in its composition (Belskaya et al., 2015). The object of the study was the systems based on MgAl- and MgGa-LDH. Our previous works demonstrated that platinum catalysts supported on magnesium-aluminum oxides, which are obtained from the corresponding LDH, are promising catalytic systems for dehydrogenation of light and higher alkanes (Belskaya et al., 2016a, 2016b, 2015; Stepanova et al., 2016, 2013). Partial or complete replacement of aluminum by gallium leads to modifying of the Pt active sites properties expressed in increase of the activity of platinum catalysts based on the Ga-containing LDH while maintaining high selectivity in propane dehydrogenation. This is mainly explained by suppression of the reactions of the hydrogenolysis of C–C bonds. (Belskaya et al., 2016b). At the high temperature stage (350–450 °C) of reduction Pt–Ga interaction occurs, that allows to modify the disperse and catalytic properties of platinum. The formation of bimetallic particles occurs with the participation of gallium atoms closest to platinum (traditionally the content of platinum in the catalyst is 0.3 wt.%) and does not significantly affect its surface concentration in the support.

2. Experimental procedures

2.1. Synthesis of LDH

MgAl- and MgGa-LDH with the molar ratio $\text{Mg}/\text{M}^{3+} = 2$ were synthesized by coprecipitation (Miata, 1975). To this end, an aqueous

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