

CHEMICAL KINETICS
AND CATALYSIS

Studying Hydrotalcite-Like Compounds Isomorphically Substituted with Iron and Cobalt via Inverse Temperature-Programmed Reduction

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Abstract—The reducibility of multicomponent layered double hydrotalcite-like hydroxides containing Mg^{2+} , Co^{2+} , Al^{3+} , and Fe^{3+} at different ratios of these metal cations and products of their thermal destruction in a hydrogen flow is studied via inverse temperature-programmed reduction (iTPR). It is shown that the temperature-programmed reduction profiles for layered double hydroxides (LDHs) contain signals corresponding not only to the reduction of iron and cobalt cations incorporated into the structure of brucite-like layers, but also ones corresponding to the reduction of cobalt and iron from the mixed oxides or spinel-like phases that appear due to the thermal destruction of LDHs occurring simultaneously with a reduction in iTPR measurements. Signals presumably corresponding to the reduction of residual nitrate anions are also revealed in iTPR profiles.

Keywords: layered double hydroxides, inverse temperature-programmed reduction, cobalt, iron

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INTRODUCTION

Layered double hydroxides (LDHs) correspond to the general formula $M_{1-x}^{2+}M_x^{3+}(\text{OH})_2(\text{A}^{n-})_{x/n} \cdot m\text{H}_2\text{O}$. LDHs have a brucite-derived structure. Some doubly-charged cations are isomorphically replaced with triply charged cations, so the brucite-like layers acquire an excess positive charge compensated for by interlayer A^{n-} anions. The interlayer space also accommodates water molecules that help to stabilize this layered structure. The most studied member of this class of compounds is hydrotalcite $Mg_6Al_2(\text{OH})_{16}\text{CO}_3^{2-} \cdot 4\text{H}_2\text{O}$ [1, 2]. Other compounds of this class are mainly considered to be products from the partial or complete replacing

of magnesium and/or aluminum in the hydrotalcite structure and are frequently referred to as hydrotalcite-like compounds [3–5]. The structure of LDHs is shown in Fig. 1.

The interest in layered hydroxides is due to the possibility of using them in different fields. Hydrotalcite is the only natural anion exchanger, and its synthetic analogs also exhibit pronounced ion-exchange and sorption properties. Hydrotalcite-like compounds can be used as, e.g., catalysts and their precursors, and as medical agent carriers [6–8]. LDHs containing transition metal cations in the structure of brucite-like layers or interlayer anions are of the greatest importance for catalysis. In most cases, catalysts synthesized on

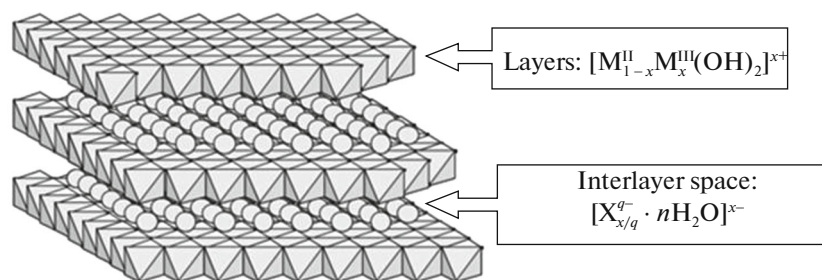


Fig. 1. Structure of layered double hydroxides [5].

Table 1. Content of cobalt and iron cations in LDHs*

Sample	α_{Co}	α_{Fe}	M^{2+}/M^{3+}	Co^{2+} , wt %	Fe^{3+} , wt %
MgCo/AlFe-1	0.16	0.14	2.37	8.0	2.7
MgCo/AlFe-2	0.31	0.26	2.6	14.8	4.6
MgCo/AlFe-3	0.56	0.54	1.90	22.4	10.8

* α_{Co} is the fraction of cobalt among doubly charged metal cations; α_{Fe} is the fraction of iron among triply charged metal cations.

the basis of LDHs are subjected to thermal treatment in a reductive atmosphere to form finely dispersed metal particles incorporated into an oxide matrix [9–12]. In this context, studying the reducibility of layered double hydroxides and determining the optimum conditions for their pretreatment become especially important.

There are some examples of the best characteristics relative to monometallic catalysts being characteristic of samples containing bimetallic pairs, e.g., nickel and cobalt or cobalt and iron [13]. Samples of bimetallic pairs in an oxide matrix can also be synthesized from LDH precursors. The aim of this work was to study the reducibility of layered double hydroxides containing doubly charged cobalt and triply charged iron ions in the structure of brucite-like layers alongside magnesium and aluminum.

EXPERIMENTAL

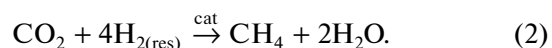
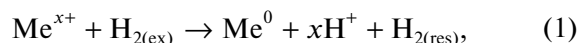
Layered double hydroxides MgCo/AlFe were synthesized via coprecipitation of compounds from solutions at variable pH and room temperature by adding a precipitant solution (molar ratio NaOH : $\text{Na}_2\text{CO}_3 = 8 : 1$) to a solution containing $\text{Mg}(\text{NO}_3)_2$, $\text{Co}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, and $\text{Fe}(\text{NO}_3)_3$. The contents of metal cations in the synthesized samples, determined with semiempirical calculations based on the data set from an energy-dispersive analysis of the content of metal cations and data from a thermogravimetric analysis [14], are given in Table 1.

The resulting precipitate was subjected to aging. It is known that if a solution contains two or more types of anions, one of them is incorporated into the LDH structure more than the other [3]. The stage of exchange was nevertheless included for carbonate anions to ensure more complete removal of nitrate anions. After this exchange, the samples were washed with distilled water and dried.

The structure and phase composition of the synthesized samples of layered double hydroxides were identified via X-ray diffraction on a Rigaku diffractometer (CuK_α radiation) with a scanning step of $2\theta = 0.02^\circ$. The content of metal cations in the synthesized samples was determined using the energy-dispersive

analyzer of a QUANTA 3D scanning electron microscope at a working voltage of 20 kV.

The reducibility of layered double hydroxides and the products of their thermal destruction was studied via inverse temperature-programmed reduction (iTPR) [15, 16]. The hydrogen flow rate was determined with a flame ionization detector (FID), improving the sensitivity of this technique relative to the classic TPR variant, in which a thermal conductivity detector is used. The gases leaving the reactor were mixed with carbon dioxide and passed through an additional reactor filled with catalyst for the hydrogenation of carbon dioxide to methane using the hydrogen not spent during the reduction of the studied samples. The scheme of the process is



The resulting methane was detected with FID. Its amount was proportional to the content of hydrogen in the mixture, allowing for the stoichiometry of reaction (2). The system was calibrated against hydrogen before and after the reaction.

To perform measurements, 25 mg of each sample were placed into a U-shaped quartz reactor. A gas mixture containing 5 vol % of H_2 in N_2 was passed through a reactor filled with the sample at a flow rate of 50 mL/min. In iTPR, the reactor is heated in the 30 to 800 or 900°C range of temperatures at a linear heating rate of 10 K/min. The flow rate of carbon dioxide used to convert the hydrogen not spent in reducing the samples to methane was 2 mL/min.

To study the reducibility of the products of thermal LDH destruction, they were preliminarily treated directly in the reactor in a nitrogen atmosphere. Each sample was heated at a rate of 10 K/min to 100, 300, and 600°C, respectively, and then hold at a specified temperature for 1 h and cooled to room temperature for subsequent inverse temperature-programmed reduction.

The samples used for comparison were synthetic hydrotalcite obtained in the form of $\text{Mg}/\text{Al}-\text{NO}_3^-$ nitrate by a procedure similar to the ones described above, but using a NaOH solution as the precipitant as well as the samples prepared by impregnating commercial Puralox MG 70 hydrotalcite (Sasol) in carbonate form with aqueous $\text{Fe}(\text{NO}_3)_3$ and $\text{Co}(\text{NO}_3)_2$ solutions containing the required amount of the abovementioned salts with the subsequent removal of water (Fe/Puralox and Co/Puralox).

RESULTS AND DISCUSSION

The powder X-ray diffraction patterns of our layered hydroxide samples are shown in Fig. 2. All of the X-ray diffraction patterns contain only the reflections

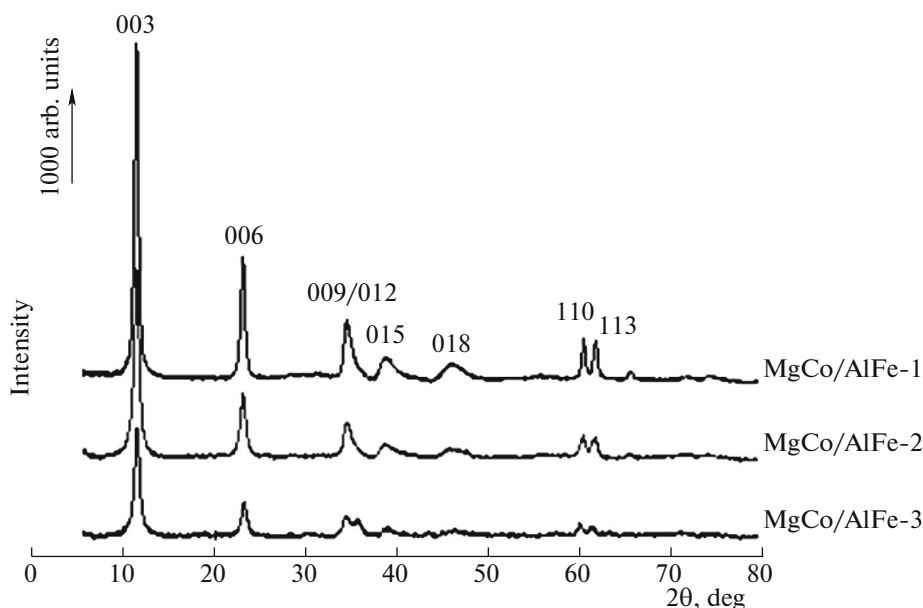


Fig. 2. X-ray diffraction patterns of MgCo/AlFe-LDHs.

typical of hydrotalcite-like compounds [3, 4]: a set of five basal reflections (003), (006), (009/012), (015), and (018) in the order of increasing diffraction angle 2θ . The intensity of the peaks falls as the diffraction angle grows. At large angles (more than 56°), the sixth and seventh reflections form a doublet corresponding to basal reflections (110) and (113). However, the intensity of the signal is seen to fall as the contents of cobalt and iron in the samples grows, possibly indicating the deformation of the crystal lattice and/or disordering of brucite-like layers as larger cations are introduced into their structure (Mg^{2+} , 0.071 ± 0.003 nm; Co^{2+} , 0.074 ± 0.002 nm; Al^{3+} , 0.051 ± 0.003 nm; Fe^{3+} , 0.062 ± 0.003 nm [17]).

The iTPR profiles of multicomponent layered double hydroxides are shown in Fig. 3. It can be seen that all of the hydrogen consumption signals are broad and poorly separated, and the base line does not return to the initial position in the investigated range of temperatures, complicating quantitative calculations of the degree of metal cation reduction. The content of metal cations that can be reduced in a hydrogen flow is low in the synthesized samples (Table 1), so they were studied at the maximum iTPR sensitivity. Due to the formation of mixed oxides, the reduction of metal cations was accompanied by solid-phase diffusion, preventing the formation of sharp and clearly distinguishable signals in the temperature-programmed reduction profiles. With iron and cobalt, the formation of different phases with various temperatures of reduction is possible.

Three regions of hydrogen consumption can be distinguished in all of the iTPR profiles. The first temperature region lies in the ~ 80 to 300°C range of tem-

peratures. The second covers the temperatures from 300 to 550°C , and the third is located above 550°C . The origin of low-temperature signals in the iTPR profiles of LDHs is not obvious. We may hypothesize that the absorption of hydrogen in the iTPR profiles of the initial LDHs (Fig. 3) in the temperature range of 80 to 300°C was due to the reduction of interlayer anions contained in the structure of LDHs. Carbonates were the dominant anions in the studied samples. Opinions on the possibility of reducing carbonate anions are contradictory. It was noted in [18] that two low-intensity peaks, attributed by the authors to the reduction of intercalated CO_3^{2-} anions and Ni^{2+} ions not incorporated into the structures of layers, respectively, can be observed for the reduction of initial NiAl-LDH in the region of low temperatures at 270 and 310°C . According to the data in [19], however, no reduction of carbonate anions is observed for the NiAl-LDH and NiMgAl-LDH samples.

In this work, the temperature-programmed reduction of LDHs was performed with subsequent mass-spectrometric detection of the gaseous products of reduction. Our mass spectra contained only the signals from CO_2 , NO , and H_2O . Our data allowed us to attribute the hydrogen consumption signal in the TPR profile in the temperature range of 227 to 327°C to the reduction of NO_3^- to NO . Similar results were given in [20] for Co-Al and Co-Mg-Al-LDH reduced without pretreatment. After Co-Al-LDH was calcined at 350°C , the mass spectrum recorded during reduction was observed to contain only trace amounts of NO , due to the nearly complete destruction of NO_3^- during calcination at this temperature. The NO signal was in turn observed in the mass spectrum of the Mg-Co-

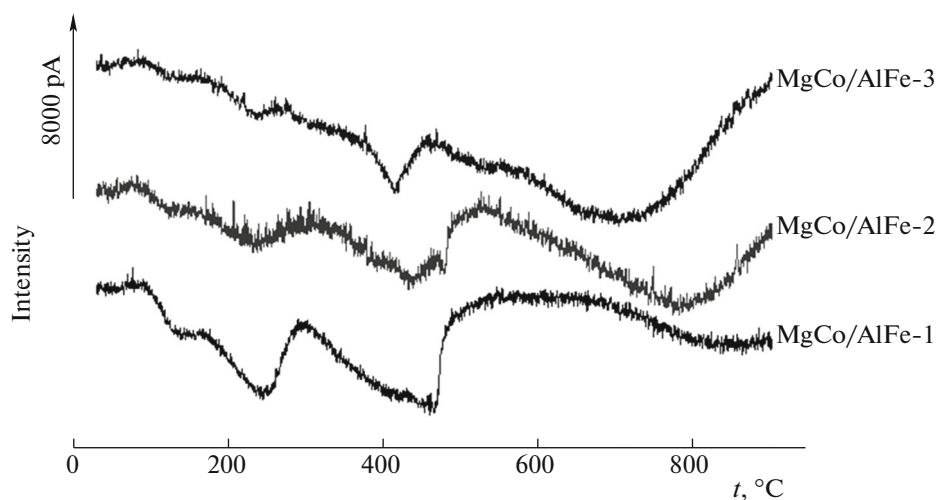


Fig. 3. iTPR profiles for MgCo/AlFe-LDHs.

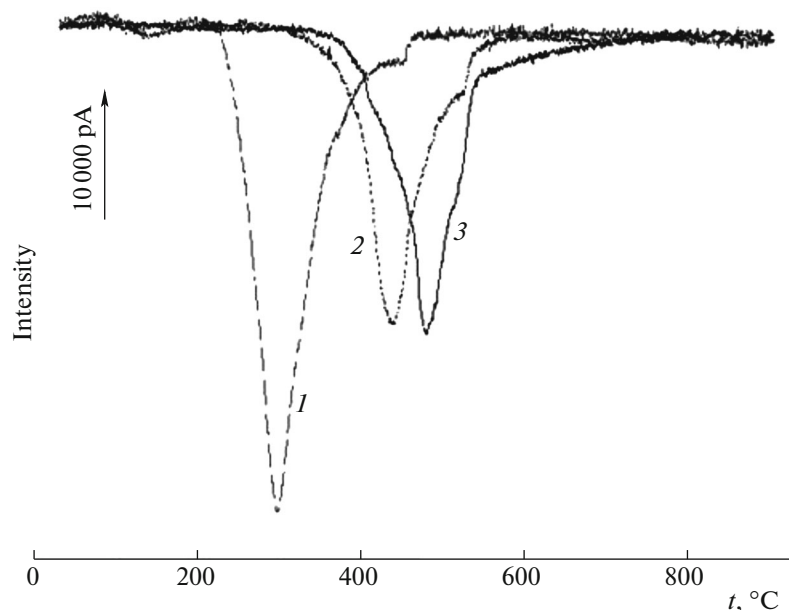


Fig. 4. iTPR profiles for reference samples (1) 7.6% Co/Puralox MG 70, (2) 2.7% Fe/Puralox MG 70, and (3) Mg/Al-NO₃⁻.

Al-LDH sample even after calcination at 350°C, and disappeared completely only after calcination at 500°C. We assume this was due to the higher thermal stability of NO₃⁻ and CO₃²⁻ at increased contents of magnesium ions.

To confirm the reducibility of nitrates in the above-mentioned range of temperatures, NO₃⁻-containing reference samples similar to synthesized MgCo/AlFe-LDHs in terms of structure and cationic composition were studied via iTPR. The reference samples were synthetic hydrotalcite Mg/Al in nitrate form (Mg/Al-NO₃⁻) and samples prepared by impregnating commercial synthetic hydrotalcite Mg/Al in the

carbonate form with solutions of cobalt and iron nitrates (7.6% Co/Puralox MG70 and 2.7% Fe/Puralox MG 70). The contents of cobalt and iron in the prepared samples was close to those of the corresponding cations in the synthesized MgCo/AlFe-1 LDH. The iTPR profiles of the reference samples without preliminary treatment are shown in Fig. 4.

All of our iTPR profiles contained an intense broad non-symmetric signal. With Mg/Al-NO₃⁻, the presence of such an intense signal clearly shows the consumption of hydrogen in the temperature range of 330 to 730°C with an absorption maximum at 475°C is due to the reduction of NO₃⁻. In terms of hydrogen con-

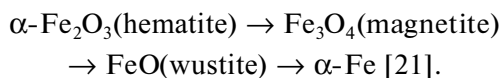
sumption, we may assume the products of reduction contain not only NO, as was noted in [19, 20], but N₂ as well. The calculated amounts of consumed hydrogen for the 7.6% Co/Puralox MG70 and 2.7% Fe/Puralox MG70 samples also considerably exceeded those required for the reduction of cobalt and iron, respectively. To all appearances, the consumption of hydrogen in these samples was due to the reduction of the corresponding metals and NO₃⁻. It should be noted that the temperature of the maximum rate of hydrogen consumption depended largely on the cationic composition of the samples. The presence of iron shifted the maximum of hydrogen consumption for 40°C toward lower temperatures, relative to the Mg/Al–NO₃⁻ sample. The presence of cobalt in turn led to a greater drop in the temperature of NO₃⁻ reduction. The maximum rate of hydrogen consumption in this sample shifted for 180°C toward lower temperatures, relative to Mg/Al–NO₃⁻.

Comparing the literature data and our iTPR results for the initial MgCo/AlFe–LDHs and the reference samples, we may assume that the consumption of hydrogen in the low-temperature region was due to the reduction of residual nitrate anions. Since this is a multi-electron process, nitrates produce intense peaks even in trace amounts. Nitrate reduction can proceed with the formation of different products, e.g., NO and N₂.

Small amounts of NO₃⁻ in the structure of MgCo/AlFe–LDHs are possible, since nitrates of the corresponding metals were used to synthesize our LDH samples and some might have remained even after ion exchange for carbonates [19].

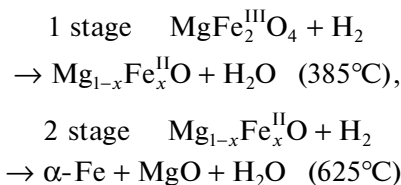
The nature of hydrogen consumption in the medium- and high-temperature regions (Fig. 3) is more obvious: it is due to the processes of iron and cobalt reduction. The signals in the temperature range of 300 to 550°C represent the superpositioning of several signals; Co²⁺ and Fe³⁺ ions are most likely reduced in different environments (aluminum or magnesium). The reduction of Co²⁺ ions to Co⁰ proceeds in a single stage. Iron ions are in turn capable of stage-wise reduction, first to doubly-charged cations and then to Fe⁰, and this could also contribute to the complicated shape of the signal.

The reduction of the bulk α-Fe₂O₃ phase proceeds as

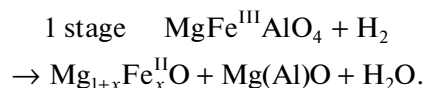


With LDHs, the reduction of iron cations is complicated by their interaction with magnesium and aluminum cations and the possible formation of different solid solution phases, e.g., MgFe₂O₄, Mg(Al,Fe)₂O₄, (Mg,Fe)Al₂O₄, and Fe₃O₄ during iTPR analysis. Since inverse temperature-programmed reduction is a kinetic technique, the diffusion of hydrogen through the oxide phase could lead to broadening of the signal.

As follows from the data in Fig. 3, not all of the cobalt and iron cations are subjected to reduction in the intermediate range of temperatures. Broad regions of high-temperature hydrogen consumption are clearly seen in the iTPR profiles. This too is likely due to the formation of mixed oxides or spinel-like phases during the thermal treatment of LDHs. The reduction of cobalt and iron from similar phases is known to be complicated [22, 23]. According to [22], CoO thus gives the sole narrow signal at ~337°C; CoAl₂O₄ is reduced at much higher temperatures, and the reduction maximum is observed at 887°C. The rise in the temperature of cobalt reduction from spinel is explained by aluminum ions polarizing the Co–O bonds, thereby raising the energy of the lattice. It is also known that the reduction of cobalt from the Mg(Co,Al)O solid solution begins at a temperature above 700°C with a maximum at 870–887°C, thus indicating strong interaction between CoO and Mg(Al)O [23]. A similar picture is observed for the reduction of iron cations. According to the data in [24], Fe₂O₃ is reduced to Fe₃O₄ at ~297°C, and the reduction of Fe₃O₄ to Fe⁰ is observed at ~497°C. In [25], it was noted that magnesium cations inhibits iron reduction. We therefore propose the following two-stage scheme of iron reduction from the products of Mg₇₀Fe₃₀ LDH thermal destruction:



With the products of Mg–Al–Fe–LDH thermal destruction, we note the presence of broad and overlapping peaks shifted toward higher temperatures in the TPR profiles and assume that the second stage of reduction begins before the first stage ends. We consider the first stage to be the partial reduction of Fe³⁺ to Fe²⁺:



We consider the second stage as described above. As noted in this work, however, the temperature of iron reduction in the first and second stages in the Mg–Al–Fe–LDH series depends largely on the content of magnesium, aluminum, and iron cations. It varies from 409 to 473°C in the first stage and from 737 to 789°C in the second.

To verify the above hypotheses of LDH reduction, products of LDH treatment at different temperatures were studied via iTPR (Fig. 5). The data presented in Fig. 5 show that thermal treatment at 100°C results in the disappearance of the signal at the lowest temperature, which lies below 170°C. The most intense signal with a maximum at 250°C disappears completely after

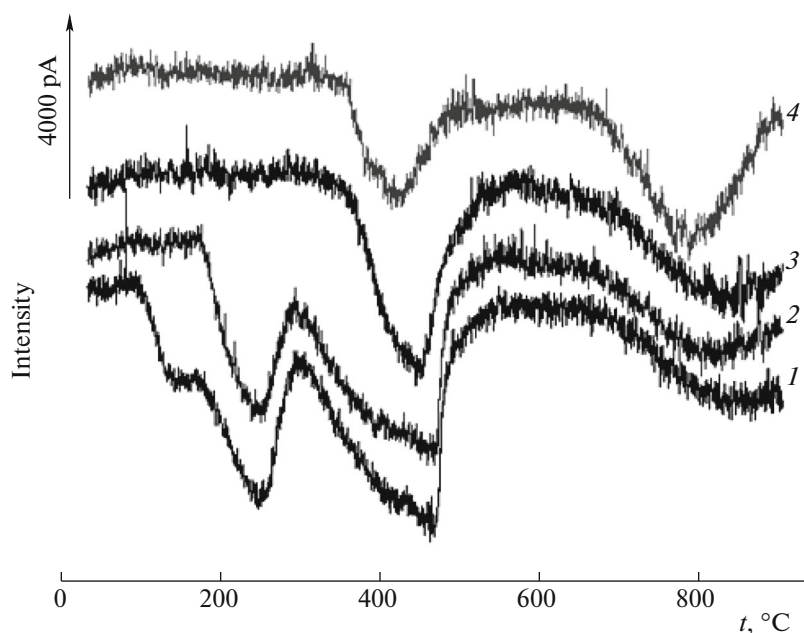
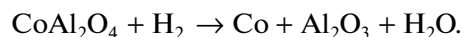
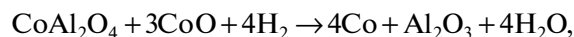


Fig. 5. iTPR profiles for MgCo/AlFe-1 (I) in the initial state and after thermal treatment at (2) 100, (3) 300, and (4) 600°C.

thermal treatment at 300°C in the low-temperature region. Our data thus agree with the hypothesis that the residual nitrate anions removed due to the collapse of the layered structure during the thermal treatment of LDH samples are reduced in this region. However, we cannot exclude the possibility that the disappearance of the signal in the low-temperature region at a higher temperature of pretreatment could also have been due to conversion leading to the disappearance of easily reducible forms of metals.

The data acquired during the temperature-programmed reduction of LDHs subjected to thermal treatment at fairly high temperatures also agree with the hypothesis regarding the formation of spinel phases. The thermal treatment of LDHs at 600°C lowers the intensity of the hydrogen consumption signal in iTPR in the 330 to 550°C range of temperatures and raises the intensity of the signal in the high-temperature region (above 550°C). The hydrogen consumption maxima also shift. The results we obtained for our mixed tetrametallic layered hydroxides and their products of thermal destruction are in good agreement with the data in [26], where we studied bimetallic cobalt-containing LDHs. In addition to the low-temperature hydrogen absorption signals produced by the two-stage reduction of the Co_3O_4 phase ($\text{Co}_3\text{O}_4 \rightarrow \text{CoO}$ and $\text{CoO} \rightarrow \text{Co}$), the oxides we synthesized in [26] via the thermal treatment of CoAl-LDH also displayed a high-temperature signal that was attributed to the reduction of CoAl_2O_4 with a maximum at ~660–680°C and a shoulder at 520–600°C. We propose the following scheme of CoAl_2O_4 reduction:



In this work, the temperature of cobalt spinel reduction was slightly lower than in [23] for the Mg(Co,Al)O solid solution, the reduction of cobalt from which began at a temperature above 700°C. This could have been due to there being no magnesium in the structure of the hydroxide precursor from [26]. It must also be considered that the temperature of reduction depends strongly on the conditions of a TPR experiment and sample pretreatment.

CONCLUSIONS

Signals in the region of high temperatures can definitely be attributed to the reduction of Co^{2+} and Fe^{2+} ions incorporated into the spinel-like phase formed during the simultaneous reduction and thermal destruction of LDHs. Our results show that bimetallic pairs can be synthesized in an oxide matrix via the reduction of layered double hydroxides with no pretreatment.

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