Mg-Cu-Al LAYERED DOUBLE HYDROXIDES BASED CATALYSTS FOR THE REDUCTION OF NITRATES IN AQUEOUS SOLUTIONS

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The secondary waste and bacterial contamination in physico-chemical and biological separation processes used today for nitrate removal from ground water make novel catalytic technologies that convert nitrates to unharmful gaseous nitrogen, very attractive for scientific research. The Mg-Cu-Al layered double hydroxide (LDH) based catalysts with different Mg/Al ratio were investigated in water denitrification reaction in the presence of hydrogen and with solely copper as an active phase. Since LDHs have ion exchange properties and their derived mixed oxides possess memory effect (restoration of layered structure after thermal decomposition), their adsorption capacity for nitrates was also measured in the same model system. All studied samples showed nitrate removal from 23% to 62% following the decrease in Al content, as well as the substantial adsorption capacity ranging from 18% to 38%. These results underlie the necessity to take into account the effects of the adsorption in all future investigations.

KEYWORDS: Mg-Cu-Al anionic clays, nitrate removal, nitrate adsorption, water denitrification

INTRODUCTION

Nitrate concentration in drinking water supplies in many world regions (EU, USA, Canada, India, etc.) has increased in the last decade (1, 2). Due to its high toxicity, removal of nitrate has become an environmental issue (2, 3, 4), which has increased the drinking water quality standards (50 mg/L in the European Union and 25 mg/L in the USA) (1, 4). Effective removal of nitrate ions from ground water is presently achieved by conventional physicochemical methods like ion exchange, reverse osmosis and electrodialysis. However, generation of undesirable nitrates reach secondary waste streams, as a draw-back of these methods, raises a need for the development of new technologies (1, 3). Selective reduction of nitrates to nitrogen is the most environment friendly method for nitrates removal and can be realized by biological digestion and catalytic reduction. The most widely used denitrification process today is biological denitrification; however, possible bacterial contamination, the presence of residual organics and the possible increase in chlorine demand in purified water limit the application of this process (3). Therefore

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the catalytic reduction of nitrates appears as the best solution because of efficient chemical reaction, flexibility, simple configuration of the reactor, etc. In this catalytic process, nitrate ions are reduced using hydrogen and converted into nitrites as an intermediate, while nitrogen, hydroxyl ions and ammonia are the final products (3). The advantage of layered double hydroxides (LDHs) based catalysts is their ability to concentrate first the NO$_3^-$ ions from water solution in the LDH interlayer, and after complete conversion to OH$^-$ and either N$_2$ or NH$_4^+$, exchange OH$^-$ ions left in the interlayer with new NO$_3^-$ ions from the solution and start another catalytic cycle (1). Typically, metal-oxide supported bimetallic catalysts, combining a noble metal, usually Pd or Pt, and another metal, such as Cu, Sn, or In, supported on alumina have been applied for this reaction (1, 3-6).

The LDHs, also called anionic clays or hydrotalcite like materials, have brucite-like layers consisting of octahedrally coordinated M(II) ions surrounded with OH$^-$. When some M(II) ions are isomorphically substituted with M(III) ions a positive layer charge is induced and compensated by the anions in the interlayer. Since there is no limitation to the nature of interlayer anions, these anions can be exchanged, resulting in a substantial anion exchange capacity of the LDH. After thermal decomposition/calcination of LDHs the layered structure collapses and mixed oxides are formed having an interesting property called “memory effect”, an ability to restore the original layered structure in contact with water and different anions. This property is the basis for the high adsorption capacity of LDHs. Due to the possibility to tailor catalytic properties of LDHs by varying their composition, synthesis method and parameters, LDHs are suitable catalyst supports (7, 8). When loaded with Pd and Cu, these catalysts have shown high activity in the reaction of nitrate reduction, which makes them very attractive for further scientific studies (1, 3, 5). The catalytic activity of copper in LDHs as sole active phase has not been investigated so far, which justifies the present study. In order to estimate the net effect of the catalytic reduction, the adsorption capacity of LDH based catalysts was also measured in the same model system, without the presence of hydrogen.

**EXPERIMENTAL**

For the synthesis of LDHs of the general chemical formula [M(II)$_{1-x}$Al$_x$(OH)$_2$][(CO$_3$)$_x$/2]$_y$H$_2$O (where M(II) are divalent ions (Mg, Cu); x is the ratio between Al content and the total metal content), low supersaturation method has been chosen, explained in detail elsewhere (9). The composition of metals was chosen inside and outside the optimal range (0.25<x<0.33) for the single phase LDH synthesis, with the intention to compare single phase and complex, multiphase, metastable systems. The loading of Cu as the active component, constant in all samples, was 10 mol%. The constant flow of 4 ml min$^{-1}$ of Mg(NO$_3$)$_2$·6H$_2$O, Cu(NO$_3$)$_2$·6H$_2$O and Al (NO$_3$)$_3$·9H$_2$O in aqueous solutions with the total molar metal amount $n_{Mg} + n_{Al} + n_{Fe} = 1$ mol, was introduced to the distilled water and vigorously stirred (300 rpm). The constant pH value (pH 9.7-10.2) was maintained by adding of Na$_2$CO$_3$ and NaOH solutions.

The chosen denotation of samples shows the starting amount of all constituting metals in molar percent. For example, the sample with starting 60 mol% of Mg, 10 mol% of Cu
and 30 mol% of Al is denoted as Mg 60-Cu 10-Al 30. The calcined samples have an additional letter C, for example C-Mg 75-Cu 10-Al 15.

X-ray diffraction analysis (XRD) was used to determine the phase composition and crystal structure using Seifert MZ-IV diffractometer (anticathode CuKα wavelength: λ=0.15406 nm, halt time 60 s, at 40 kV and 55 mA) in 2θ range from 5° to 70°.

The morphology of the samples was studied by scanning electron microscopy (SEM) using JEOL, JSM-6460LV instrument, at the working voltage of 20 kV and working distance of 10 mm.

The same instrument was used for the qualitative and preliminary quantitative analysis of mixed oxides surface by energy dispersive spectroscopy (EDS).

Preceding the reaction catalyst precursors were calcined 5h at 500°C and then reduced/activated in a hydrogen flow (60 ml min⁻¹) at 200°C during 2h. Finely powdered catalyst samples (0.2 g) were introduced into a pyrex batch reactor and mixed with 100 ml of aqueous nitrate solution (KNO₃) with NO₃⁻ concentration of 100 mg dm⁻³ (100 ppm). The mixture was stirred with magnetic stirrer (350 rpm) at room temperature and saturated with hydrogen at a constant flow of 50 cm³ min⁻¹ (Brooks Instruments Division, Emerson Electric CO, USA flow controller). After 1 h of reaction time, the hydrogen flow was stopped, the catalyst was separated using Hettich, Rotofix 32 centrifuge (2200 rpm, 5 min) and the remaining solution was used to determine the concentration of nitrate, nitrite and ammonium ions. The Jenway ionselective electrode was used to determine the nitrate ion concentration and Cole-Palmer ionselective electrode for ammonium ion concentration. UV-VIS CECIL CE 2021 2000 Series spectrophotometer was used to measure nitrite ion concentration at 538 nm, applying the ISO 2918:1975 referent method. Catalysts performance is presented as NO₃⁻ conversion and selectivity towards undesirable product NH₃, calculated as the ratio of NH₃ concentration and conversion.

The adsorption experiments were performed applying the same catalyst-adsorbens/solution ratio, following the same model solution concentration and temperature, as well as identical conditions of adsorption and separation sequences as used in the catalytic tests excluding the presence of hydrogen.

RESULTS AND DISCUSSION

The diffractograms (Fig. 1) show the presence of characteristic LDH patterns (7, 9) in all as-synthesized samples, sharp, symmetric (003), (006), (110) and (113) reflections and asymmetric (102), (105) and (108) peaks. In the sample Mg 60-Cu 10-Al 30, synthesized within the optimal range for the single LDH synthesis (0.22 <x < 0.33), having the most intensive XRD peaks, only the LDH phase was identified. The same was found in the case of the sample Mg 75-Cu 10-Al 15 having the Al content near to the optimal range. In the samples Mg 40-Cu 10-Al 50 and Mg 20-Cu 10-Al 70, with the enhanced Al amount, besides the LDH phase, an additional aluminum phase, Bayerite - Al(OH)₃, was observed. The reflections of the other single hydroxide, Mg(OH)₂ and Cu(OH)₂, were not detected in any sample regardless of metals loading. It was observed that with an increase in the departure from the optimal metals range for single LDH phase synthesis the intensities of XRD patterns characteristic for LDH phase decreased.
Figure 1. XRD patterns of as-synthesized samples
(+ - LDH phase, * - Bayerite (Al(OH)_3) phase)

After the calcinations and in accordance with previous investigations (9, 10), the layered structure collapses with the formation of mixed oxides solid solution (Fig. 2). In all samples, only the characteristic patterns of mixed oxides, MgCu(Al)O, with regular, dense-packed, cubic, NaCl-type oxygen lattice were observed, with decreasing intensities following the increase in the aluminum content. The characteristic XRD patterns of additional aluminum or copper phases were not detected after calcinations/thermal decomposition of samples.

Figure 2. XRD patterns of calcined samples (o – mixed oxide Mg(Al)O phase)
Morphology of of calcined samples was analyzed by SEM. The images given in Fig. 3 indicate the presence of agglomerates of plate-like particles connected at the edges at various angles. The size of particles and agglomerates within the studied series varied depending on sample composition. The dimensions of particles decreased with the increase in Al content, which is in accordance with the results of our previous investigation (9, 10) showing that aluminum ions act as nucleation centers during the coprecipitation.

The EDS analysis detected the presence of Mg, Cu, Al and O in all samples. Considerable amounts of C, N and Cl were also present, implying the necessity for a prolonged calcination and more excessive washing of the synthesis solution, to eliminate carbonates and nitrates. The presence of Cl probably originates from the poorly distilled water used for washing. In order to give a quantitative analysis of surface composition, multiple EDS analysis per sample, having statistically valid analysis of several surface spots is necessary.

![SEM micrographs of calcined Mg -Cu -Al samples, magnification 50 000 x](image)

**Figure 3.** SEM micrographs of calcined Mg -Cu -Al samples, magnification 50 000 x

The results of catalytic and adsorption efficiency are presented in Fig. 4 show the values for both catalytic reaction possibly coupled with adsorption and sole adsorption. The catalytic nitrate conversion, ranging from 23% to 62%, depends on the catalyst composition, decreasing with the increase in aluminum content. All samples also show a substantial NO$_3^-$ adsorption capacity, ranging from 18% to 38%. The highest catalytic conversion and the lowest adsorption capacity was observed for the Mg 75-Cu 10-Al 15 catalyst having the lowest amount of Al. In contrast, the Mg 20-Cu 10-Al 70 catalyst, with the highest amount of Al, has the lowest catalytic conversion and the highest adsorption capacity. The result is a bit ambiguous, showing a negative effect of the presence of hydro-
gen on the adsorption efficiency ($\text{NO}_3^-$ depletion due to the catalysis coupled with possible simultaneous adsorption is lower compared to the sole adsorption). This may indicate that some catalyst properties change in the hydrogen environment, which may not be preferential for $\text{NO}_3^-$ adsorption. However, the conclusion about the possible mechanism of adsorption hindering in the presence of hydrogen should be based on a more detailed investigation of the observed phenomena. The best catalytic performance in the studied series of Mg-Cu-Al LDH-based catalysts were observed for the samples having single LDH phase precursors (Mg 75-Cu 10-Al 15 and Mg 60-Cu 10-Al 30). It could be concluded that the larger amount of aluminum and the presence of an additional Al phase besides LDH phase in the catalyst precursors has a negative effect on the catalyst behavior. That is in accordance with the earlier explained mechanism of water denitrification on LDHs-based catalysts, in which the LDH phase is the sole environment for the catalytic cycle.

For a detailed analysis of catalytic activity, a supplementary investigation of redox and acid-base properties are required. Substantial adsorption capacity underlies the necessity to take into account the effects of adsorption in all future investigations.

![Figure 4. Nitrate removal due to catalytic reduction and adsorption](image)

Besides nitrate ion reduction the concentrations of products other than nitrogen (nitrite and ammonium ions) were also measured, as well as the pH value at the end of the reaction (Fig. 5). The presence of traces of nitrite ion in all samples regardless of their composition (in the range from 0.685 to 1.025 ppm) shows that nitrate to nitrite reduction as the first intermediate step of the reaction, is not a limiting step. This step may have happened on the copper active site, with different activities for the constant Cu concentration explained by various active site environments (different Mg/Al ratio). The following $\text{NO}_2^-$ transformation, either to desirable nitrogen or to harmful NH$_3$ may have happened on other active sites belonging to Mg or Al phases as it seems that various Mg/Al ratio in different samples may be responsible for different NH$_3$ concentrations (Fig. 5). It has to be mentioned, however, that such dramatic changes in the Mg/Al ratio (from 75/15 to 20/70) bring only small differences in the absolute amount of NH$_3$ produced, as shown in Fig. 5. Nevertheless, substantial selectivity differences, measured by factor of 4 and mo-
re, occur due to the substantial changes in NO$_3^-$ conversion among catalyst samples (Fig. 5). Thus, the least selective catalyst towards undesirable ammonia (please note this is the best catalytic performance), was the sample with the lowest amount of Al, Mg$_{75}$-Cu$_{10}$-Al$_{15}$, which also exhibited the highest NO$_3^-$ conversion. In general, selectivity to ammonia increased with the increase in Al content.

![Figure 5](image_url)

**Figure 5.** Total amount of NH$_3$ produced and selectivity towards NH$_3$. (corresponding pH values have been measured at the end of the reaction)

The achieved selectivity towards ammonia in relation to pH observed at the end of the reaction (Fig. 5) should also be discussed. The problem of high pH conditions as favorable for the enhanced NH$_3$ production has been discussed in the literature (11) and correlated to the catalyst pore structure (12). It was noticed that diffusion restricted OH$^-$ ions, produced in the course of the reaction, may temporarily block active sites and diminish the catalyst activity. Besides, they can impose a permanent pH-gradient inside the small pores, making suitable conditions for the nitrite transformation to ammonia. Also, a high specific surface area coupled with beneficial mesopore size has been shown in our previous work as a prerequisite for both high activity and high selectivity (13, 14). The performance of the most active and selective catalyst sample, Mg$_{75}$-Cu$_{10}$-Al$_{15}$, corresponds to the mentioned studies, at least when the observed pH value is concerned. This sample shows advantageous performances working at the highest pH in a series, which could be a consequence of an efficient exchange of OH$^-$ ions inside of LDH layers by NO$_3^-$ . Thus the majority of produced OH$^-$ ions is driven out of the LDH interlayer into the water solution, leaving new NO$_3^-$ reactant near active sites under the favorable pH conditions for desirable NO$_2^-$ transformation to N$_2$. In contrast, in the case of samples with additional Al phases, OH$^-$ ions remain trapped inside the pores cavities, pushing the reaction towards NH$_3$ production. A detailed textural characterization is required in order to prove the mechanism leading to the observed selectivity differences. Also, for a further investigation it could be recommended to confirm the results using another analytical method for the measurement of the nitrate and ammonium ions concentration because the measurements with the ionselective electrodes are very sensitive and tentative.
CONCLUSION

The synthesis of Mg-Cu-Al layered double hydroxides having 10% Cu and different Mg/Al ratios was successful, as confirmed by XRD analysis. In the samples with a composition having substantial deviation from optimal single LDH phase synthesis, an additional aluminum phase, Bayerite-Al(OH)₃ was identified. The morphology of the samples depends on sample composition. All samples have agglomerates of plate-like particles with dimensions decreasing with the increase in Al content. EDS analysis detected the presence of Mg, Cu, Al and O in all samples, as well as a considerable amount of C, N and Cl, suggesting that prolonged calcination and more excessive washing of synthesis solution are needed to eliminate carbonates and nitrates from the samples. All studied samples were active in the catalytic nitrate reduction reaction with hydrogen, showing NO₃⁻ reduction from 23% to 62%, following the decrease in Al content. The highest conversion was measured for the single-phase samples with high amounts of magnesium and potential base properties. All studied samples showed substantial adsorption capacity, ranging from 18% to 38%. For the future investigation, it would be necessary to take into account the effects of the adsorption. It should be noted that Mg-Cu-Al LDHs have been successfully used as a catalyst support with palladium as active phase. The observed activity of Mg-Cu-Al LDHs based catalysts showed that the support also has a catalytic function and that careful design of Mg-Cu-Al with Pd as active phase may lead to very efficient catalysts for the studied reaction.

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REFERENCES


КАТАЛИЗАТОРИ НА БАЗИ Mg-Cu-Al СЛОЈЕВИТИХ ХИДРОКСИДА ЗА РЕДУКЦИЈУ НИТРАТА ИЗ ВОДЕНИХ РАСТВОРА

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Секундарни отпад и контаминација бактеријама, присутни код тренутно заступљених физико-хемијских и биолошких процеса сепарације нитрата из водених раствора, чини нове катализитичке технолошке које конвертују нитрата до нештетног гасовитог азота интересантним за истраживање. Катализатори на бази Mg-Cu-Al слојевитих хидроксида (LDH) са различитим Mg/Al уделима су испитивани у реакцији денитрификације у присуству водоника са само бакром као активном фазом. Пошто LDH имају јоноизменичајачки капацитет, а њихови мешовити оксиди поседују ефект памћења (врећање слојевите структуре након термичког разградње), испитиван је и адсорпциона капацитет у односу на нитрате у истом модел систему. Сви узорци су показали уклањање нитрата од 23% до 62% које прати опадање Al садржаја, као и значајни адсорпциона капацитет у опсегу од 18% до 38%. Ови резултати истичу неопходност узимања у обзир ефекта адсорпције при свим будућим истраживањима.

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