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A study of thermally activated Mg–Fe layered double hydroxides as potential environmental catalysts

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Abstract: Layered double hydroxides (LDHs) and mixed oxides derived after thermal decomposition of LDHs with different Mg–Fe contents were investigated. These materials were chosen because of the possibility to tailor their various properties, such as ion-exchange capability, redox and acid–base and surface area. Layered double hydroxides, $[Mg_{1\text{-}x}Fe_x(OH)_2](CO_3)_{x/2}\cdot mH_2O$ (where x presents the content of trivalent ions, x = M(III)/(M(II) + M(III)) were synthesized using the low supersaturation precipitation method. The influence of different Mg/Fe ratios on the structure and surface properties of the LDH and derived mixed oxides was investigated in correlation to their catalytic properties in the chosen test reaction (Fischer–Tropsch synthesis). It was determined that the presence of active sites in the mixed oxides is influenced by the structural properties of the initial LDH and by the presence of additional Fe phases. Furthermore, a synthesis outside the optimal range for the synthesis of single phase LDHs leads to the formation of metastable, multiphase systems with specific characteristics and active sites.

Keywords: Mg–Fe–LDHs; hydrotalcite; anionic clays; Mg–Fe mixed oxides; Fischer–Tropsch reaction.

INTRODUCTION

In recent years, many investigations have been focused on the development of low-cost heterogeneous materials with basic characteristics that could be used in reactions for industrial purposes. Layered double hydroxides, LDHs, are anionic clays that also known as hydrotalcite-like materials
$([M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A_{x/n})^{n-}\cdot mH_2O)$,
where x represents the content of trivalent ions, x = M(III)/[M(II) + M(III) and A^{n-} is the anion. LDHs are formed by isomorphic substitution of octahedrally

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coordinated M(II) cations in brucite-like layers with trivalent cations. The positive charge is compensated by hydrated anions located in the interlayer space together with water forming the layered structure. The properties of LDHs and of thermally derived mixed oxides can be tailored by variation of the M(II), M(III) cations and interlayer ions and different M(II)/M(III) ratios, resulting in their wide application as acid-base and redox catalysts, catalyst supports, anion exchangers, adsorbents *etc*. The synthesis of single-phase LDHs is narrowed to the range $0.2 \leq x \leq 0.33$.[1,2] The influence of the extent of M(III) substitution (within and outside the optimal range), on surface properties of LDHs and derived mixed oxides and their efficiency as catalysts in the Fischer–Tropsch test reaction were investigated. The conversion of syngas (CO + H_2 mixtures) to a range of hydrocarbons using Fischer–Tropsch synthesis (FTS) is currently of increasing interest in the scientific field. The FTS products are complex mixtures of organic compounds that depend on the catalysts employed, as well as on the operating conditions. Therefore, selectivity of catalysts towards the desired products is of great importance. Magnesium was chosen as the M(II) ion, because of its basic properties, and iron as the active M(III) ion, because of its reductive characteristics and its ability to form specific active sites in the layered structure required for catalytic application.[3]

EXPERIMENTAL

Layered double hydroxides were synthesized using the low supersaturation co-precipitation method at constant pH with different Mg:Fe ratios and x in the range 0.15–0.7. Precursors with different Mg:Fe atomic ratios were prepared using aqueous solution of $Mg(NO_3)_2\cdot6H_2O$ and $Fe(NO_3)_3\cdot9H_2O$ continuously (4 cm^3 min^{-1}) added at constant pH (*ca*. 9.6–9.9) maintained by simultaneous addition of Na_2CO_3 and NaOH solution. The products of the precipitation were calcined for 5 h in air at 500 °C.

Structural analysis (XRD) of LDH and mixed oxide samples was investigated with a Siemens D500 X-ray diffractometer (Cu Kα radiation, $\lambda = 0.154$ nm, 45 kV, 25 mA) in the 2θ range from 3 to 63°. The texture of mixed oxides was evaluated by low temperature nitrogen sorption at −196 °C using a Micromeritics ASAP 2010 instrument.

The investigation was oriented to the selectivity of the synthesized samples because their selectivity towards particular hydrocarbons is of essential importance in evaluating their potential in the overall activity in FTS. Selectivity tests were performed in a tubular reactor. The catalysts were activated by reduction treatment with a pure hydrogen flow of 20 ml min^{-1} for 2 h at 350 °C. The gas flow was adjusted by mass flow controllers with the H_2:CO ratio of 2:1. The entire reactor system was placed inside a furnace at a temperature of 375 °C. Reaction products were analyzed using a gas chromatograph, HP 5890, Series II, equipped with TCD and FID detectors. The selectivity of the prepared catalysts was calculated using the following formula (S – selectivity, F – detector response factor, x – desired product, nC – number of C atoms in the product; A – value of the surface under the peak):

$$S = 100\frac{(F_x nC_x A_x)}{\sum(F_{\text{product}} nC_{\text{product}} A_{\text{product}})} \tag{1}$$

RESULTS AND DISCUSSION

All the synthesized samples showed X-ray diffraction patterns that are typical for layered double hydroxides,[1,4] but a single LDH crystalline phase structure was observed only in the samples with x values of 0.15 and 0.3, Fig. 1. The sample with the lowest amount of Fe ($x = 0.15$) showed broad XRD lines, indicating a less ordered structure. Outside this composition range, x from 0.5 to 0.7, the XRD peaks typical for LDH decreased linearly with increasing amount of Fe in samples, corresponding to a lower crystallinity and a less ordered structure. Another crystalline Fe phase (goethite, FeO(OH)) was observed in the sample with an x value of 0.5. The typical XRD patterns for this additional Fe phase were not detected in the sample with the highest amount of Fe ($x = 0.7$), probably due to the low intensity of the peaks and the signal response noise, but its presence was also assumed in this sample.

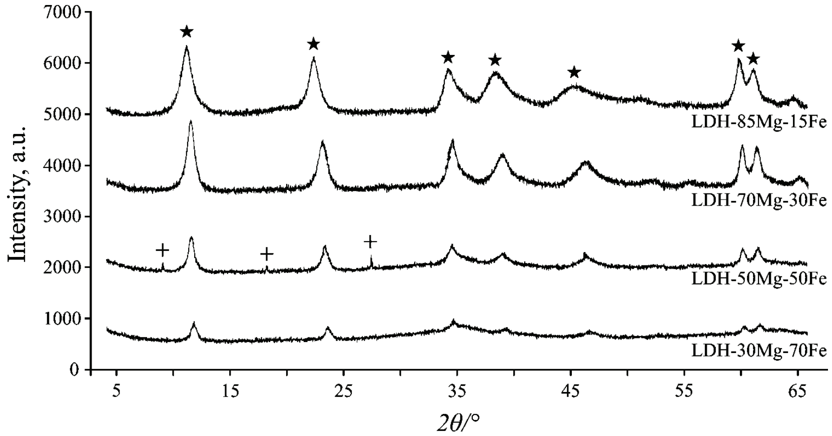

Fig. 1. XRD Patterns of all the synthesized LDH samples (★ – LDH; + – goethite).

The lattice parameters: basal spacing $d_0 = d(003)$, cation–cation distance $a_0 = 2d(110)$ and parameter $c_0 = 3d(003)$ are presented in Fig. 2. The $d(110)$ reflection is independent of the kind of layer stacking and can be utilized for the calculation of the parameter a, whereas the $d(003)$ reflection, the true c parameter, depends on the layer stacking sequence.[1] With increasing amount of Fe in the sample, a decrease in the lattice parameters, indicating a decrease in the interlayer distance and a higher attraction between the negatively charged hydroxide layers and the anions present in the interlayers, was also reported elsewhere.[5]

The XRD analysis of all the samples after thermal treatment showed diffraction peaks typical for mixed oxides with a regular, dense-packed, cubic, NaCl-type oxygen lattice, shown in Fig. 3. A collapse of the layered structure leading to the formation of mixed oxides after calcination was observed in all samples. The intensity of the XRD peaks decreased with increasing iron content in the samples and with increasing deviation from the optimal range for the single-phase synthesis. The XRD analysis of the samples synthesized with a content of Fe higher than the mentioned optimal range revealed additional phases of hematite (Fe_2O_3) and spinel ($MgFe_2O_4$).[6] The intensity of the characteristic additional phase signals increased with increasing Fe content in the samples, indicating also higher amounts of these phases in the samples with $x = 0.7$. This also confirms the mentioned assumption about the presence of the additional Fe phase in the original LDH sample.

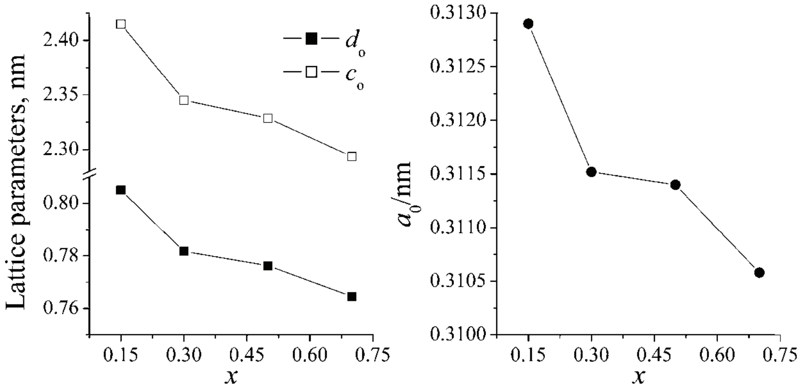

Fig. 2. The influence of the chemical composition of the LDH on the lattice parameters.

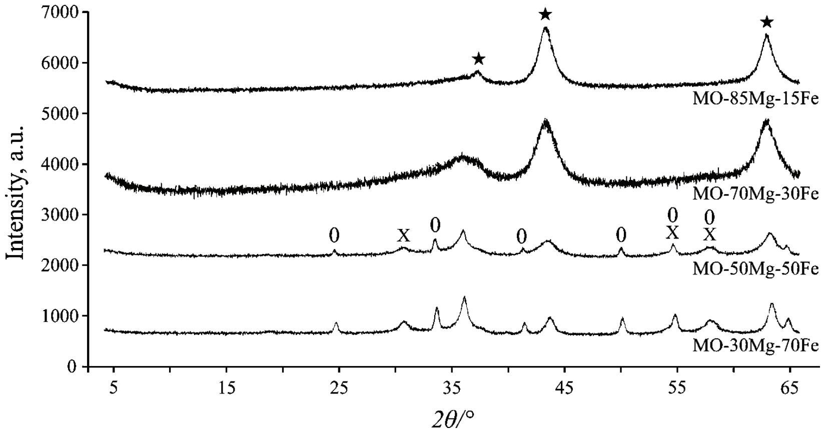

Fig. 3. XRD Patterns of the samples after thermal treatment (★ – mixed oxides; 0 – hematite, X – spinel).

The structural parameter a_0 as a function of the amount of Fe in the sample is presented in Fig. 4, from which it can be seen that the values for a_0 decreased with increasing amount of Fe in the samples.

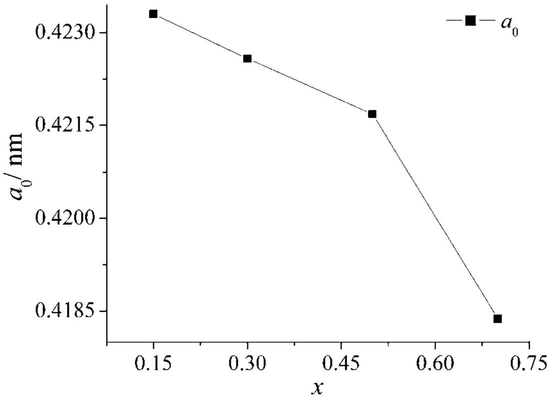

Fig. 4. Structural parameters of the mixed oxides.

The surface area of the as-synthesized LDH samples and after the thermal and reduction treatment, as well as the influence of the amount of iron in the samples is shown in Fig. 5. The increase of the surface area after thermal treatment for samples with $x = 0.15$ and 0.3 is due to the formation of smaller mesopores.[7] The presence of additional phases in samples with $x = 0.5$ and 0.7 negatively influences the development of surface area after calcination. A smaller decrease in the surface area was detected for the sample $x = 0.5$, which contained lower amounts of additional phases. The LDH sample with the highest iron content ($x = 0.7$) had the highest surface area that significantly decreased after calcination. This drastic fall was due to the lowest amount of carbonate in the LDH interlayers in this sample and the formation of additional crystalline phases identified by XRD analysis.

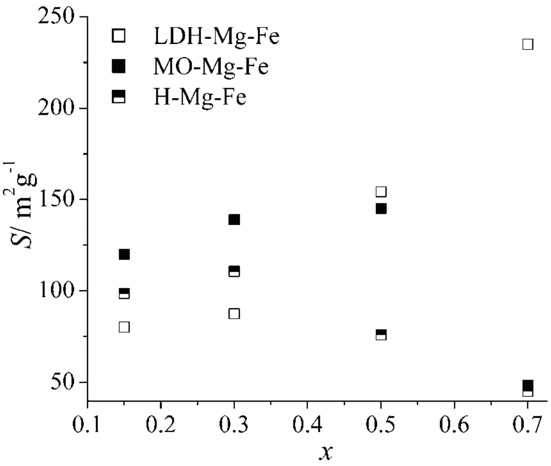

Fig. 5. Surface area of the LDH, derived mixed oxides and mixed oxides after reduction in dependence on the Fe content.

The surface area of the mixed oxides after reduction was lower than the surface area of the mixed oxides after calcination, Fig. 5, most likely due to the formation of new phases after the reduction.

The selectivity of all samples towards C_4 and C_5 products at 375 °C and a H_2:CO ratio of 2:1 is presented in Fig. 6. The sample with the lowest iron content, having the highest basicity compared to the other samples, exhibited the highest selectivity. These results are in agreement with literature data, where it was observed that with increasing MgO content in the sample, the selectivity of the Fe-catalysts in the FT reaction also increased.[8]

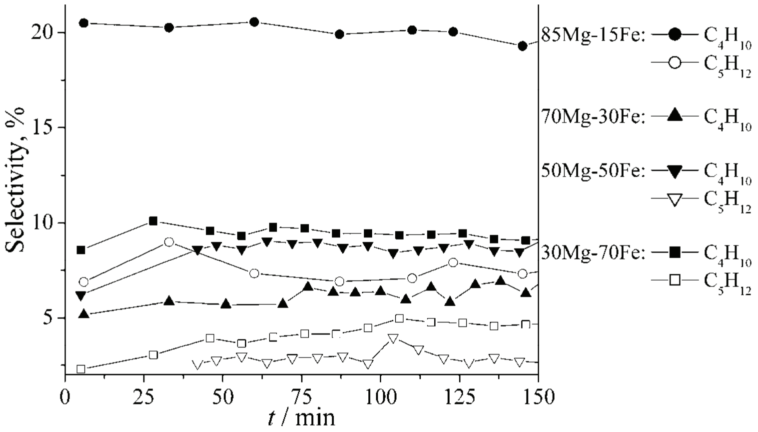

Fig. 6. Selectivity of all samples towards C_4 and C_5 products at 375 °C at an H_2:CO ratio of 2:1.

The sample synthesized in the optimal range for single-phase LDH synthesis (70 Mg–30 Fe) exhibited low selectivity towards C_4-compounds, while selectivity towards C_5-compounds was not detected. The very low selectivity of this sample is probably due to its stable structure, as observed by XRD analysis, which is not desirable for catalytic application. Both of the samples 50 Mg–50 Fe and 30 Mg–70 Fe exhibited selectivity towards C_4- and C_5-compounds. The sample with the highest Fe content showed selectivity towards C_5-compounds after 5 min of the reaction, whereas selectivity for the 50 Mg–50 Fe sample towards C_5-compounds was detected after 40 min.

CONCLUSIONS

The synthesis of Mg–Fe layered double hydroxides outside the optimal range for a single LDH phase resulted in the formation of complex, multiphase, layered double hydroxides, which gave metastable phases of oxides after thermal treatment. These mixed oxides enabled the development of active sites on the surface contributing to their catalytic performance. The reduction of mixed oxides before their application in the Fischer–Tropsch reaction decreased the surface area, most likely due to the formation of new phases. All the samples synthesized outside the optimal range for a single LDH phase showed higher selectivity towards the chosen products compared to the samples synthesized within the optimal range. The sample with the lowest iron content having the highest basicity compared to other samples exhibited the highest selectivity in the FT reaction. The stable structure of the sample synthesized in the optimal range disenabled the formation of active sites and confirmed the positive effect of metastable structures on catalytic properties. Such results open up a new route for the synthesis of LDHs with desired properties for application in certain catalytic reactions.

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ИЗВОД

ИСПИТИВАЊЕ ТЕРМИЧКИ АКТИВИРАНИХ Mg–Fe ДВОСТРУКИХ СЛОЈЕВИТИХ ХИДРОКСИДА КАО ПОТЕНЦИЈАЛНИХ КАТАЛИЗАТОРА У ЗАШТИТИ ЖИВОТНЕ ОКОЛИНЕ

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Испитивани су двоструки слојевити хидроксиди (LDHs) са различитим садржајем Mg–Fe и мешовити оксиди који су настали њиховом термичком разградњом. Двоструки слојевити хидроксиди $[Mg_{1-x}Fe_x(OH)_2](CO_3)_{x/2}\cdot mH_2O$, где је x удео тровалентних анјона, $x = M(III)/(M(II) + M(III))$ синтетисани су копреципитационом методом мале презасићености. Извршена је карактеризација мешовитих оксида насталих из LDHs, као и нетретираних LDHs, испитивањем кристалографске структуре, термичких карактеристика, текстуре, кисело–базних карактеристика и морфологије. Проучаван је утицај различитог односа Mg/Fe на структурне, површинске и кисело–базне карактеристике LDHs и њихових мешовитих оксида у корелацији са каталитичким карактеристикама у одабраној тест реакцији (Fischer–Tropsch синтеза). Утврђено је да структурне карактеристике полазног LDH, присуство додатних фаза Fe и кисело–базне карактеристике утичу на присуство активних центара код свих мешовитих оксида, као и да синтеза ван оптималног опсега за добијање једнофазних LDHs доводи до формирања метастабилних, вишефазних система са специфичним карактеристикама и активним центрима.

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