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**THE SYNTHESIS OF Zn-Al HYDROTALCITES
UNDER DIFFERENT CONDITIONS AND TESTING
IN ALDOL CONDENSATION**

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The Zn-Al hydrotalcites (materials with the layered structure) with constant molar ratio of Zn/Al 2:1 were synthesized by co-precipitation method under different reaction conditions, such as pH, the concentration of ions, temperature throughout co-precipitation, the intensity of stirring, etc. The mixed oxides were formed from hydrotalcites by calcination at 450 °C. All synthesized materials were characterized by X-ray diffraction, thermogravimetric analysis, and via the specific surface area. The influence of the synthesis conditions on the crystallite size and specific surface area were studied. The formation of hydrotalcites as well as mixed oxides was confirmed by X-ray diffraction. The mixed oxides chosen were rehydrated, which enabled to restore their layered structure. Both mixed

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oxides and rehydrated (mixed) oxides were tested in the aldol condensation of furfural, resulting in finding that the rehydration would decrease the conversion of furfural when using all the rehydrated mixed oxides.

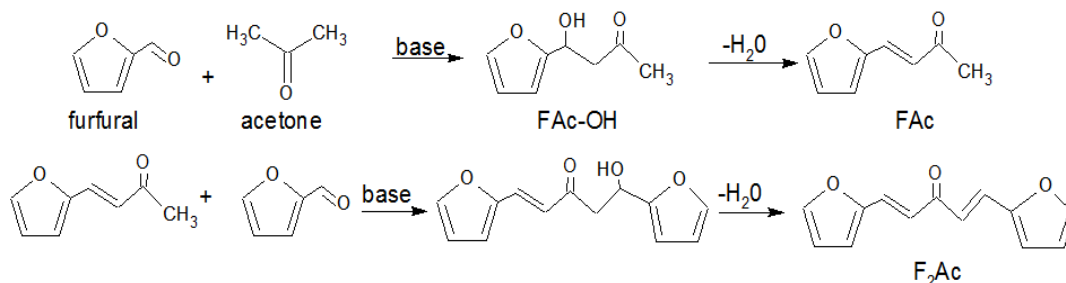
Introduction

Hydrotalcites (known as the layered double hydroxides) are frequently studied material for their easy synthesis and good acid-base properties, which can further be modified. They belong to the group of anion clays [1] with the layered structure derived from brucite – $\text{Mg}(\text{OH})_2$, where Mg^{2+} ions occupy octahedral position and form the infinite layers connected by hydrogen bonds [2]. In the hydrotalcites structure, a part of Mg^{2+} species is substituted by trivalent cations and this layer (cation layer) has a positive charge, which is compensated by anions presented in the interlayer space (anion layer) [3]. The general formula of hydrotalcite is $[\text{M}_{1-x}^{2+}\text{M}_x^{3+}(\text{OH})_2]^{x+} \text{A}_{x/n}^{n-} \cdot z\text{H}_2\text{O}$, where M^{2+} and M^{3+} are bivalent (Mg^{2+} , Zn^{2+} , Ca^{2+} , Cu^{2+}) and trivalent (Al^{3+} , Fe^{3+} , Cr^{3+}) metallic cations, respectively [4], A represents an anion (such as CO_3^{2-} , $\text{Cr}_2\text{O}_7^{2-}$, Cl^- , NO_3^-), x varies usually between 0.20-0.35 and z is the number of water molecules [5]. The combination and molar ratio of metal cation influence the structure and hydrotalcite properties. They could be prepared by hydrothermal, sol-gel or mostly co-precipitation method. The last named is carried out at the constant pH and the properties for preparation for hydrotalcite with different cations are derived from a procedure for Mg-Al hydrotalcite [6]. The co-precipitation can be influenced by many parameters, such as pH, temperature, the stirring rate, and a rate of reactants inserted to the reaction mixture [7].

The mixed oxides are formed by thermal pre-treatment (calcination) of hydrotalcite, where the (originally) Brønsted active sites are transformed into the Lewis active sites. The mixed oxides contain three types of basic active sites: weak, medium and strong [7] and can be rehydrated so that the layered structure can be restored and Lewis active sites are transformed back into Brønsted active sites that are active in the aldol condensation. The basicity of rehydrated mixed oxides is higher in comparison with hydrotalcites synthesized by co-precipitation. The reason is that the rehydrated mixed oxides contain OH^- as the compensated anions that are more basic, whereas non-rehydrated mixed oxides contain CO_3^{2-} (also compensated) being less basic. This effect is known as a memory effect [8,9].

Aldol condensation is the reaction between two molecules with carbonyl groups [10,11] enabled by homogenous catalysts; nowadays, mostly by NaOH. A basic water as a waste is formed within the separation of the main product from the catalyst. For this reaction, heterogeneous catalysts are also studied, because they can be easily separated from products and consequently reused. Furfural is a colorless viscous liquid, which is prepared by acid hydrolysis of biomass as corn

cobs, sugar cane bagasse, or rice husk [12]. The aldol condensation of furfural with acetone (scheme 1) gives rise to 4-(2-furyl)4-hydroxybutane-2-on (FAc-OH) that subsequently reacts to 4-(2-furyl)-3-butene-2-on (FAc) and 1,4-pentadiene-3-on-1,5-di-2-furanyl (F₂Ac) [13]. The products can be used after hydrogenation as biofuel of the second generation [14,15].



Scheme 1 Reaction scheme of aldol condensation of furfural

This article is focused on comparison of the synthesis parameters of Zn-Al hydrotalcite when using the co-precipitation method. The properties of Zn-Al hydrotalcites characterized by TG-MS, N₂-physisorption, and XRD were studied at different synthesis conditions (pH, temperature, the stirring rate, and a rate of reactants inserted to reaction mixture). The results were compared *via* the catalytic activity in the aldol condensation of furfural with acetone.

Materials and Methods

Preparation of Materials

The Zn-Al hydrotalcites were synthesized by the co-precipitation method in a glass reactor under the ambient conditions (25 °C). The first solution (cation solution) was prepared by the dissolution of Zn(NO₃)₂·6H₂O and Al(NO₃)₃·9H₂O in deionized water with constant molar ratio of Zn : Al = 2; the total concentration of the two cations being either 0.1 or 1.5 mol dm⁻³. The other conditions of synthesis, such as the reaction temperature, the intensity of stirring, the flow rate of addition of the cation solution and the aging time were set according to Table I. The second solution (alkali solution) was prepared by dissolving 159 g K₂CO₃ in 750 ml of deionized water.

The amount of 250 ml deionized water was put into the reactor and the cation solution added by a membrane pump (with a flow rate of 8 ml min⁻¹). The alkali solution with pH 10 was added simultaneously and the alkalinity kept constant. The resultant mixture was intensively stirred by a propeller (at 1400 rpm). After adding of the whole amount of the cation solution, the reaction mixture was

left to aging for 18 h at the same temperature and intensity of stirring. The formed hydrotalcite was filtered out and washed off by deionized water until the filtrate exhibited $\text{pH} < 7$, then dried for 24 h at 80 °C and finally granulated into the particles in a range of 250-500 μm). After, the hydrotalcites was calcined at 400 °C for 4 h with a temperature gradient of 5 °C min^{-1} .

Table I The synthesis conditions of hydrotalcites

| Reaction conditions | Value | | | |
|--|-------|-----|------|------|
| Intensity of stirring, rpm | 100 | 500 | 1000 | 1400 |
| Reaction temperature, °C | 25 | 45 | 65 | 75 |
| Flow rate of addition of cation solution, ml min^{-1} | 4 | 8 | 16 | 100 |
| Aging time, h | 0 | 2 | 7 | 21 |

Rehydration: The rehydration was carried out by water at 25 °C for 30 min and the molar ratio of mixed oxides to water was kept at 1:10. The filtered out solid material was dried for 40 min at 50 °C in a nitrogen flow. Then, the rehydrated mixed oxide was used as a catalyst.

Characterization of Zn-Al Materials

All synthesized materials were characterized by powder X-ray diffraction with the aid of JCPDS sheets [16]. X-ray diffractograms (XRD) were recorded by the Bruker AXS D8 Advance diffractometer using Cu $K\alpha$ radiation with a secondary graphite monochromator. The diffraction intensity was measured between 9° and 80°, with 2° steps. The crystallite size of hydrotalcite was calculated from the main reflection (11° and 60°) by the Scherrer formula $D = 0.9 \lambda / \beta \cdot \cos\theta$ where D is the average crystallite size (nm), 0.9 the value of the used shape factor, λ the wavelength of the used Cu $K\alpha$ radiation (0.154056 nm), β the full width at half-maximum (FWHM), and θ is the diffraction angle.

Thermogravimetric analysis (TGA) of dried HT catalysts was obtained using TA Instruments Discovery TGA operating at a heating ramp of 10 °C min^{-1} from room temperature up to 900 °C in a flow of nitrogen (20 $\text{cm}^3 \text{min}^{-1}$, Linde 3.0). Approximately 10 mg sample was heated in an open alumina ceramic crucible (70 μl). The surface area of the samples was determined from the nitrogen adsorption–desorption isotherms at liquid nitrogen temperature using an ASAP 2020 equipment (Micromeritics, USA); the specific surface area (S_{BET}) being determined by fitting the experimental data to the BET isotherm.

Aldol Condensation

The aldol condensation of furfural with acetone was carried out in a 100 ml stirred batch reactor at 50 °C. Prior to the catalytic tests, the mixture of 39.5 g acetone (dried with molecular sieve 3A) plus 6.5 g furfural (with acetone-to-furfural molar ratio of 10:1) was pre-heated to the reaction temperature of 50 °C. Afterwards, 1 g of catalyst (with grain of 0.25-0.5 mm) was added and the reaction left run for 6 h at 50 °C. Samples were withdrawn from the reaction mixture during the experiment at 5, 10, 20, 30, 40, 80, 120, 180, 240, 300, and 360 min. The catalyst was separated from the reaction mixture by filtration and the products analyzed by GC. Agilent 7890A gas chromatograph was equipped with a flame ionization detector (FID), using a HP 5 capillary column (30 m/0.32 mm ID/0.25 μm).

Results and Discussion

The Effect of Reaction Conditions on the Hydrotalcite Synthesis

The effect of the synthesis conditions on hydrotalcite and on the mixed oxides properties was studied, because of its association with the properties of materials and catalyst activity. The molar ratio of Zn : Al = 2:1 was kept constant for all the hydrotalcites.

Influence of pH: The formation of hydrotalcite in dependence of pH was studied first, measuring the respective throughout the addition of the cation solution. The slurry formed was sampled at pH 5.48, 10.30, and 10.78 and the diffractogram determined (see Fig. 1). The typical diffractogram for hydrotalcite (with double layer structure) was determined only at pH 10.78. In the case of pH 5.48 and 10.30, the typical lines for hydrotalcite were not determined and therefore the hydrotalcite not formed. All syntheses of hydrotalcite were processed in a range of pH 10.8-11.0; being typical values for Zn-Al hydrotalcite synthesis.

Influence of Temperature during the Synthesis: The hydrotalcite and also mixed oxides had been successfully synthesized at four different temperatures: 25, 45, 65, and 75 °C, which was confirmed by XRD (Figs 2a and 2b). The crystallite size for hydrotalcites increased with the increasing temperature from 21.8 nm at 25 °C to 49.5 nm at 75 °C. A higher crystallite size means faster filtration of hydrotalcite from the reaction solution. On the other hand, the specific surface area decreased (from 20.6 to 10.0 m² g⁻¹) with the increasing temperature (Table II). According to DTGA (Fig 3b), the differences occurred in the first step, where the bound water was released and the temperature increased with increasing precipitation temperature; in other words, higher precipitation temperature gave rise to a higher amount of water bound in the hydrotalcite structure. Observed were intensive

diffraction lines at 43.0° and 62.5° typical for the MgO-like phase or Zn-Al solid solution in Mg-based mixed oxide materials [17,18]. Moreover, the mixed oxides (synthesized at 25 and 75 °C) were rehydrated and TGA and DTGA determined (Figs 2c and 2d). It can be seen that the main decrease of matter was caused by water. In the case of rehydrated mixed oxides, the total loss of matter was higher than that for non-rehydrated mixed oxides being found 32 % and 38 %, respectively.

Table II List of Zn-Al hydrotalcites and their properties

| Way of synthesis | D_{003} nm | D_{110} nm | a nm | c nm | S_{BET} $\text{m}^2 \text{g}^{-1}$ |
|--------------------------|-----------------|-----------------|-----------|-----------|--|
| 25 °C | 21.75 | 17.44 | 0.307 | 2.26 | 20.6 |
| 45 °C | 31.22 | 21.56 | | 2.23 | 20.6 |
| 65 °C | 42.45 | 24.71 | | 2.65 | 16.8 |
| 75 °C | 49.48 | 32.37 | | 2.68 | 10.0 |
| 4 ml min ⁻¹ | 42.28 | 28.16 | 0.307 | 2.22 | 12.0 |
| 8 ml min ⁻¹ | 42.45 | 24.71 | | 2.27 | 16.8 |
| 16 ml min ⁻¹ | 39.84 | 30.75 | | 2.28 | 15.6 |
| 100 ml min ⁻¹ | 55.95 | 38.59 | | 2.28 | 20.2 |
| 100 rpm | 34.83 | 32.52 | 0.307 | 2.25 | 28.6 |
| 500 rpm | 34.61 | 26.90 | | 2.27 | 18.0 |
| 1000 rpm | 43.87 | 30.62 | | 2.28 | 14.2 |
| 1400 rpm | 42.45 | 24.71 | | 2.27 | 16.8 |
| 0.1 mol l ⁻¹ | 42.45 | 24.71 | 0.307 | 2.65 | 16.8 |
| 1.5 mol l ⁻¹ | 41.63 | 33.65 | | 2.74 | 17.8 |

Influence of Flow Rate of Addition of Nitrates Solution: The increase of the flow rate of addition of nitrate solution to the reaction mixture led to an increase of the crystallite size and surface area of hydrotalcites (Table II). On the other hand, there was no dependence between the flow rate of adding and crystallite size and surface

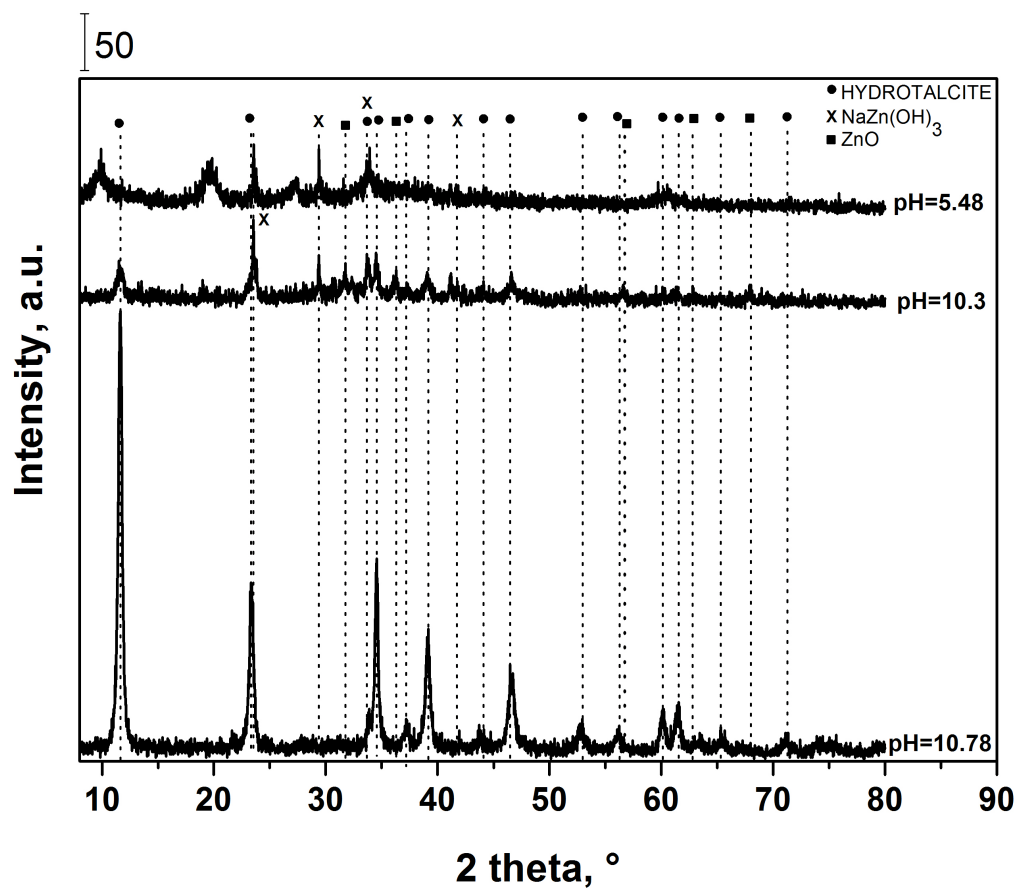


Fig. 1 XRD of the effect of preparation pH

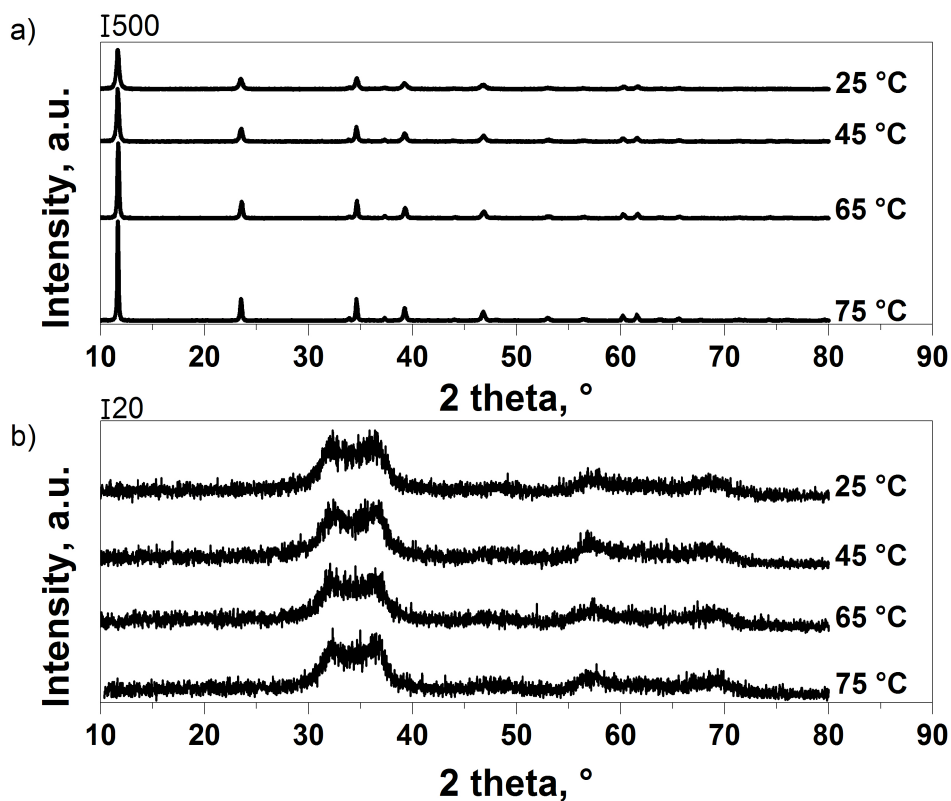


Fig. 2 XRD of synthesis hydrotalcite (a) and mixed oxides (b) at different temperatures

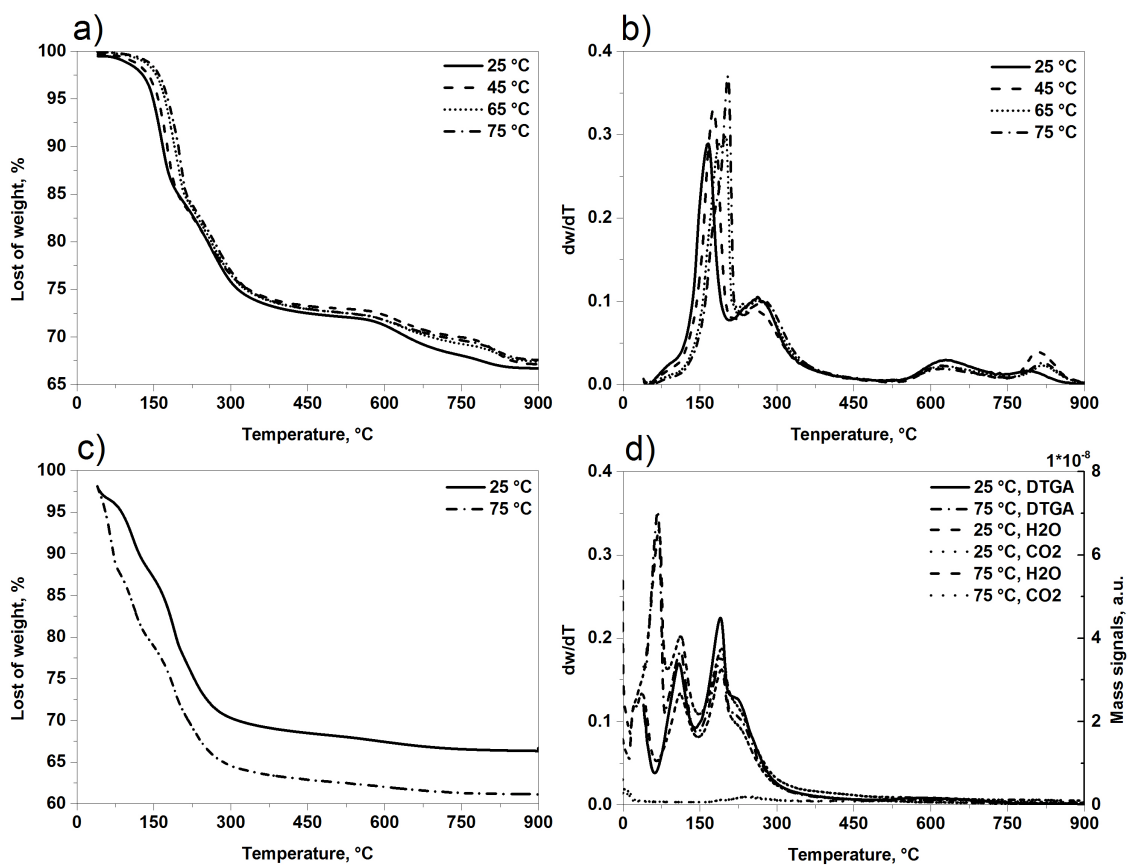


Fig. 3 TGA and DTGA of synthesis hydroxalcite at different temperatures for (a, b) mixed oxides and rehydrated (c, d) mixed oxides

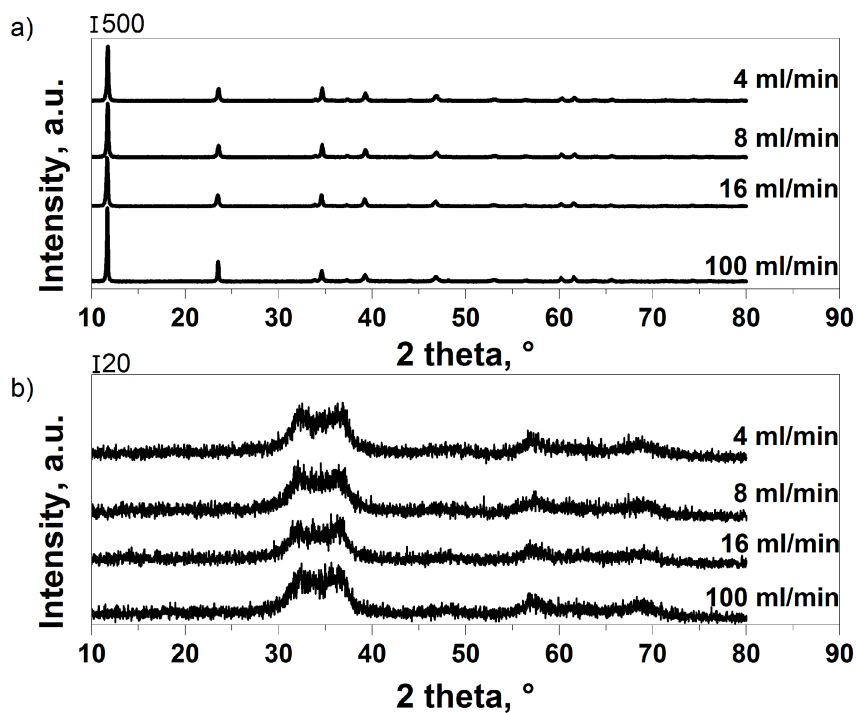


Fig. 4 XRD of synthesis hydroxalcite (a) and mixed oxides (b) at different flow rates of addition of the cation solution

area of mixed oxides. The XRD for hydrotalcites (11.7, 23.6, 34.6, 39.3, 46.9, 53.0, 56.4, 60.3, 61.6, 63.7, 65.7) and mixed oxides (32.4, 36.8, 47.7, 57.1, 68.8) is depicted in Fig 4, confirming that both materials were successfully synthesized. The TGA and DTGA curves of mixed oxides are the same for all the flow rates of addition (Figs 5a and 5b), i.e. this parameter has had no influence on hydrotalcite structure and release of the matter. The mixed oxides were also rehydrated and TGA and DTGA determined (Figs 5c and 5d). Also these results confirmed that the main loss of matter had been caused by water (removal).

Influence of Stirring Intensity of the Reaction Mixture: The XRD for hydrotalcites and mixed oxides is depicted in Fig 6. Typical diffraction lines confirmed the hydrotalcite and mixed oxides structure. The crystallite size was determined in the range from 34.6 to 43.9 nm (Table II) and, for hydrotalcite, did not depend on the intensity of stirring (from 100 to 1400 ppm). The TGA curves were almost the same for all intensities of stirring (Fig. 7) and there was no dependency between maximal temperature of the first step (approximately 200 °C) and the intensity of stirring, i.e. the intensity had no effect upon the hydrotalcite structure.

Influence of the Concentration of Metal Nitrates: The influence of the ions at two different concentrations was studied when using solutions of 0.1 and 1.5 mol l⁻¹. The hydrotalcite formed was confirmed by XRD for both concentrations and the calculated crystallite size ascertained to be almost the same: 42.5 nm for 0.1 mol l⁻¹ and 41.3 nm for 1.5 mol l⁻¹. The specific surface area was also nearly the same for both concentrations of 17.8 and 16.8 m² g⁻¹, respectively. Therefore, the hydrotalcite formed as well as the mixed oxides did not depend on the concentration of ions, which was also confirmed by TGA and being the same for both concentrations (see Fig. 9).

The comparison of the dependences studied is difficult, because the authors usually use only one set of synthesis conditions and their attention is focused mainly on the use of the respective material (and not on the synthesis). Moreover, the hydrotalcites are synthesized by many ways, such as that proposed by Muriithi *et al.* [19], who have published the hydrotalcite synthesis from a fly ash by using hydrochloride acid at various conditions, such as concentration of HCl, aging, crystallization temperature, and time.

Aldol Condensation

The mixed oxides synthesized from hydrotalcites at different conditions were tested in the aldol condensation of furfural and acetone. Moreover, the mixed oxides were also tested in the rehydrated form, when, after rehydration, the catalyst contained different amount of water in the range from 30 to 45 wt %. The conversion of furfural and selectivity to FAc-OH, FAc and F2Ac has been determined (Sche-

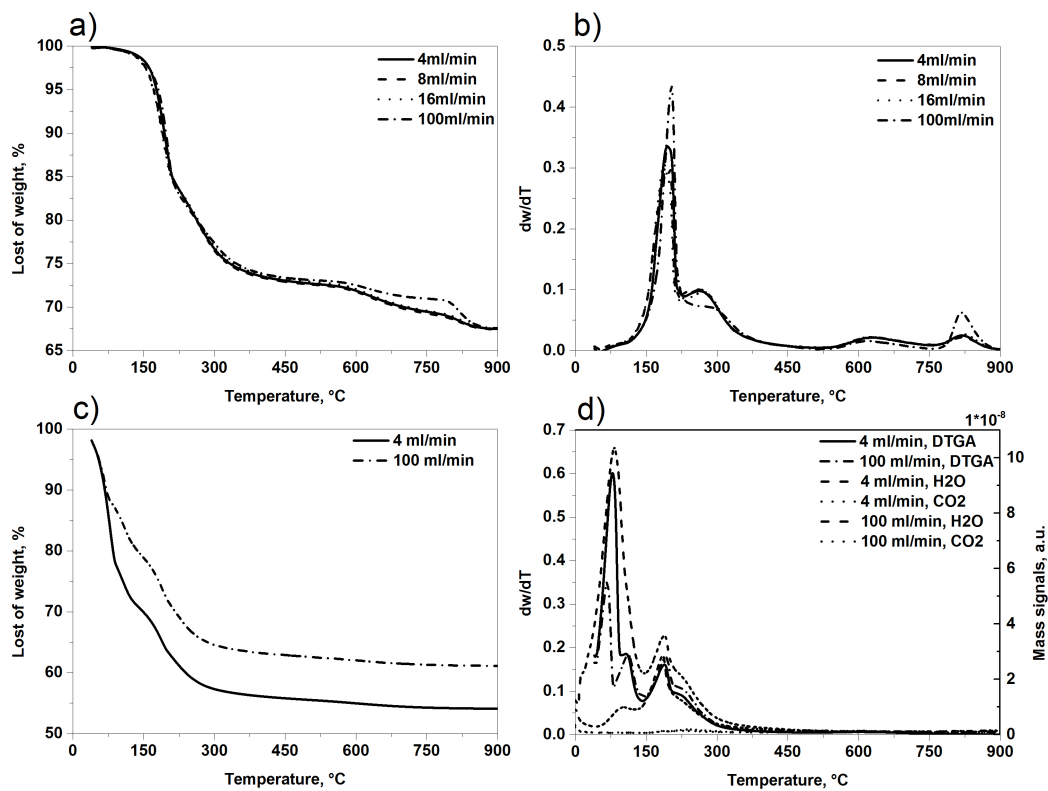


Fig. 5 TGA and DTGA of synthesis hydrotalcite at different flow rates of adding of nitrates solution for (a, b) mixed oxides and rehydrated (c, d) mixed oxides

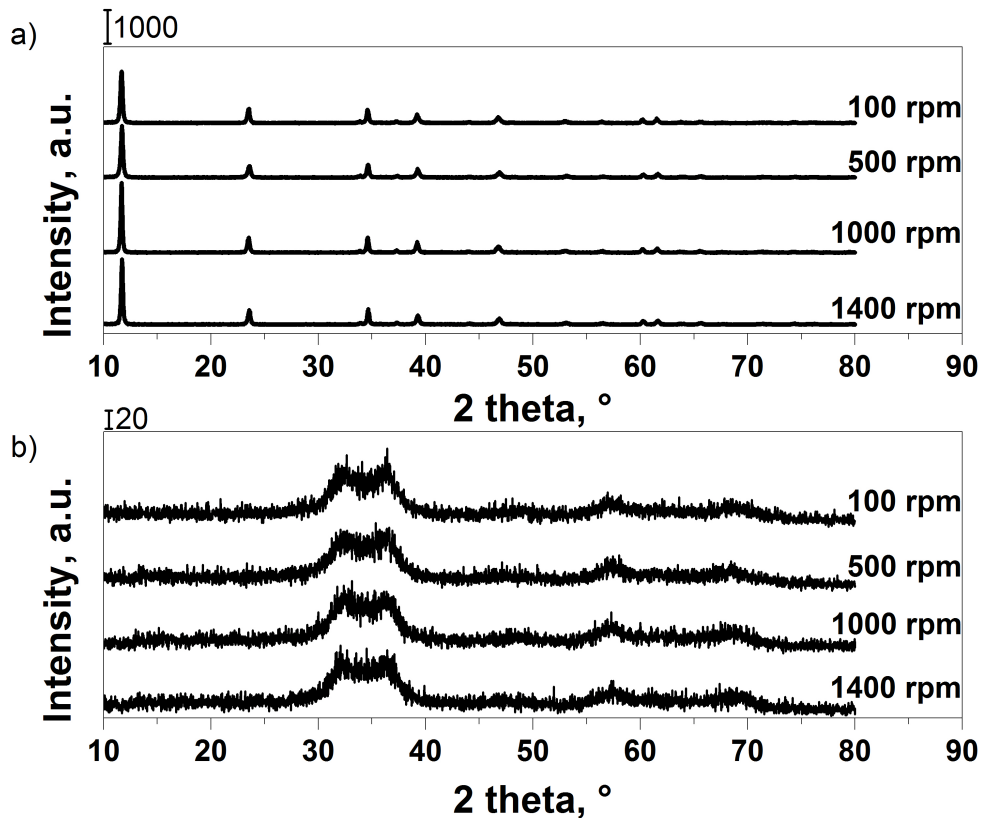


Fig. 6 XRD of synthesis hydrotalcite (a) and mixed oxides (b) at different intensity of stirring

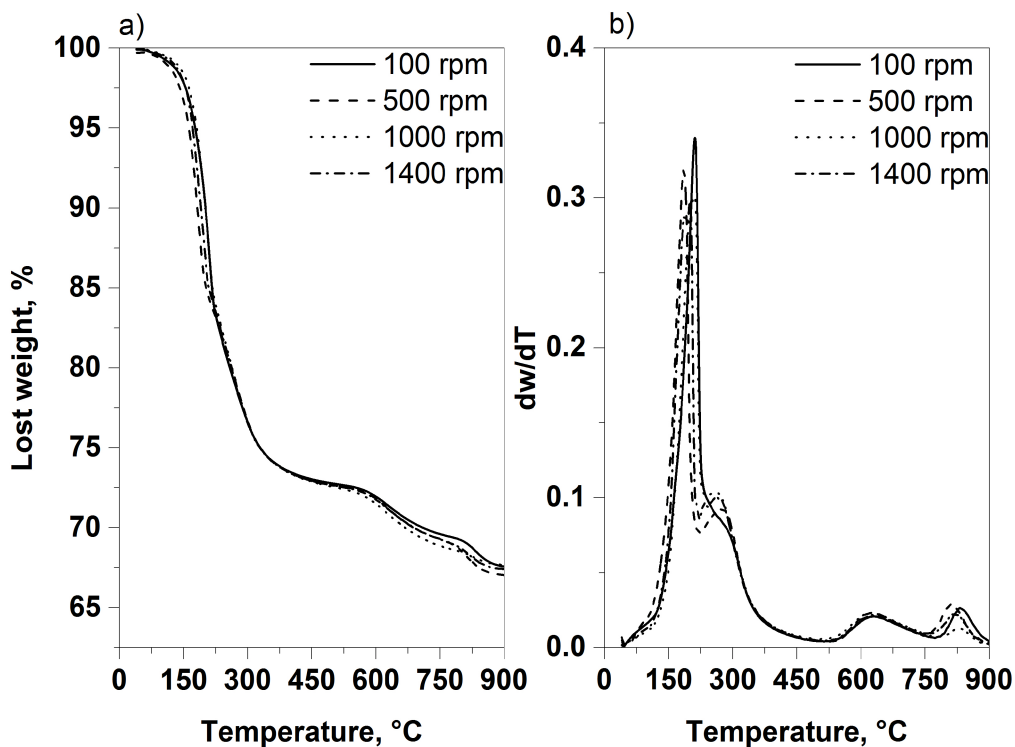


Fig. 7 TGA (a) and DTGA (b) for hydrotalcite at different intensity of stirring

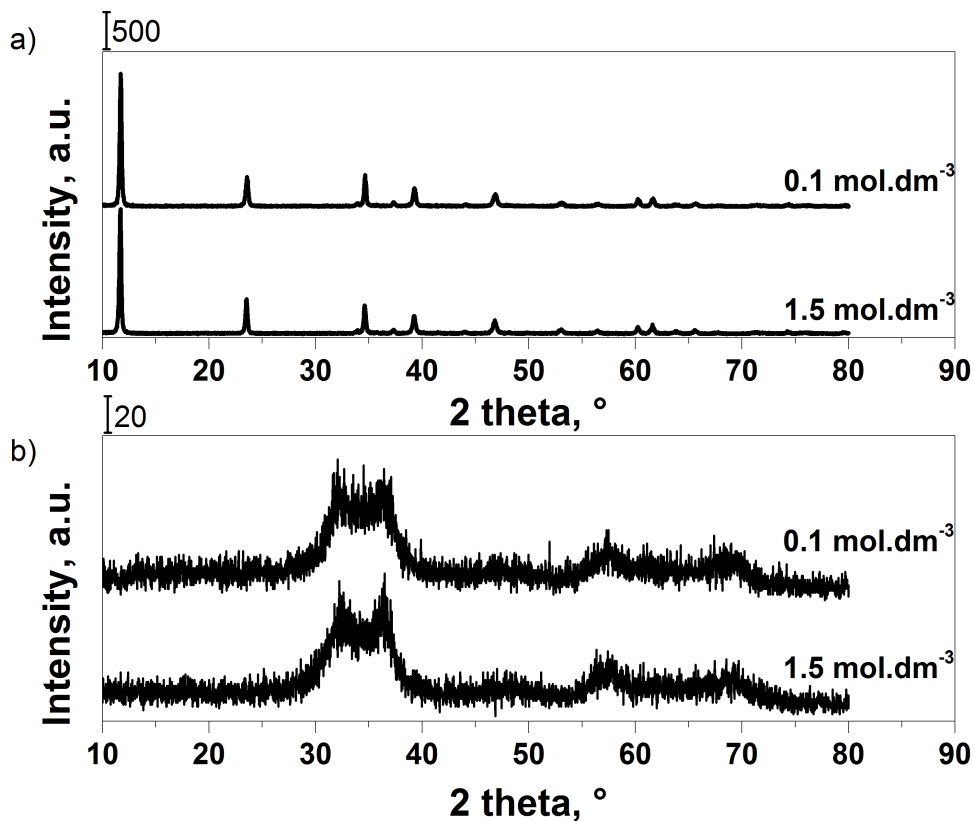


Fig. 8 XRD of synthesis hydrotalcite (a) and mixed oxides (b) at different concentration of metal nitrate

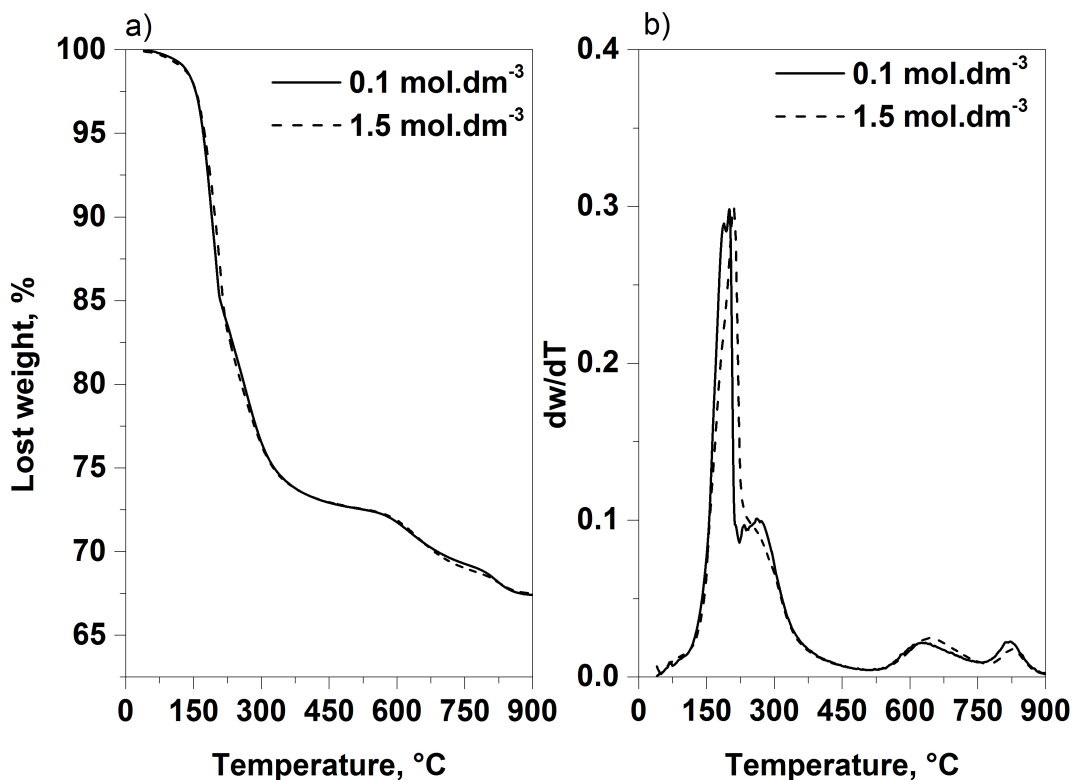


Fig. 9 TGA (a) and DTGA (b) of synthesis hydrotalcite at different concentration of metal nitrates

me 1). The results for the mixed oxides are depicted by a solid line and for rehydrated mixed oxides by a dash line in Figures 10, 11, and 12. Firstly, it should be stressed that the Zn-Al mixed oxides have achieved lower values of the furfural conversion in comparison with those for the previously studied Mg-Al mixed oxides [20], which could be caused by a lower basicity or by water adsorbed in the structure of mixed oxides. In result, the Mg-Al mixed oxides achieved conversion between 80-100 %, whereas Zn-Al much less degree, i.e. 1-13 % only.

The aldol condensation was catalyzed by the mixed oxides prepared from hydrotalcites, which were synthesized under different reaction temperatures (75, 65, 25 °C). It was found, that the decrease of synthesis temperature had had a negative influence on the furfural conversion that decreased from 13 to 8 %, respectively (see Fig 10). The mixed oxides could adsorb water formed during the reaction, because the FAc and F2Ac were formed (Scheme 1). However, the conversion by catalyst of the mixed oxides after rehydration had been yet lower: approximately 3 % for all rehydrated mixed oxides, implying that the rehydration process led to a lesser conversion degree.

Another parameter under study of the hydrotalcite synthesis was the flow rate of addition of cations solution. The mixed oxides (prepared from these hydrotalcites) and their rehydrated form were tested as catalysts (Fig. 11). The

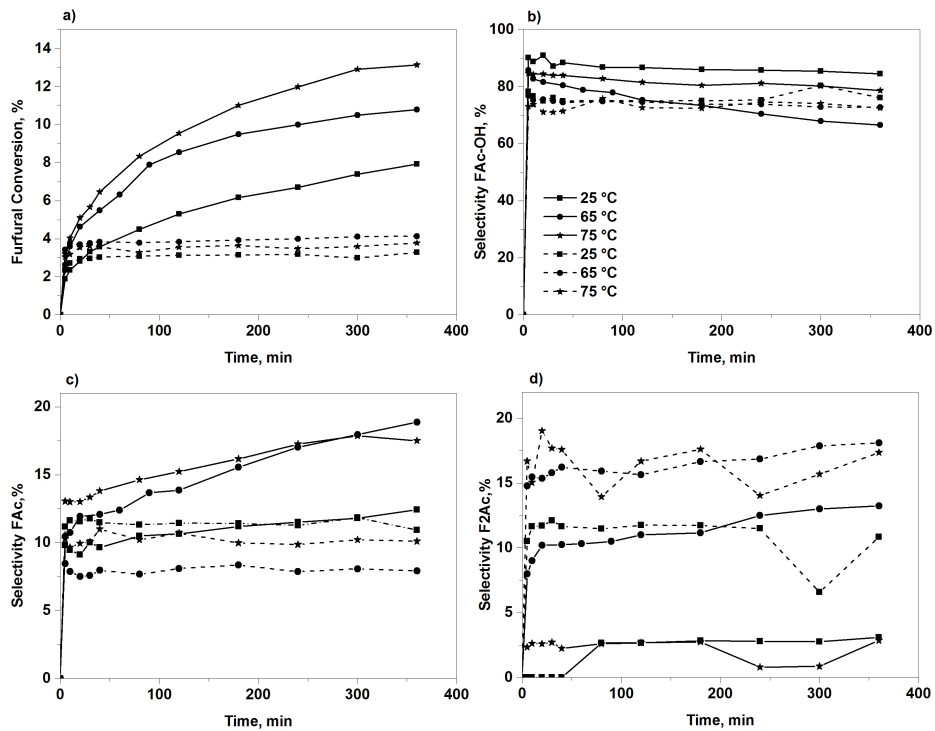


Fig. 10 The dependence of conversion and selectivity for mixed oxides synthesis at different temperature of co-precipitation (solid line) and their rehydrated form (dash line)

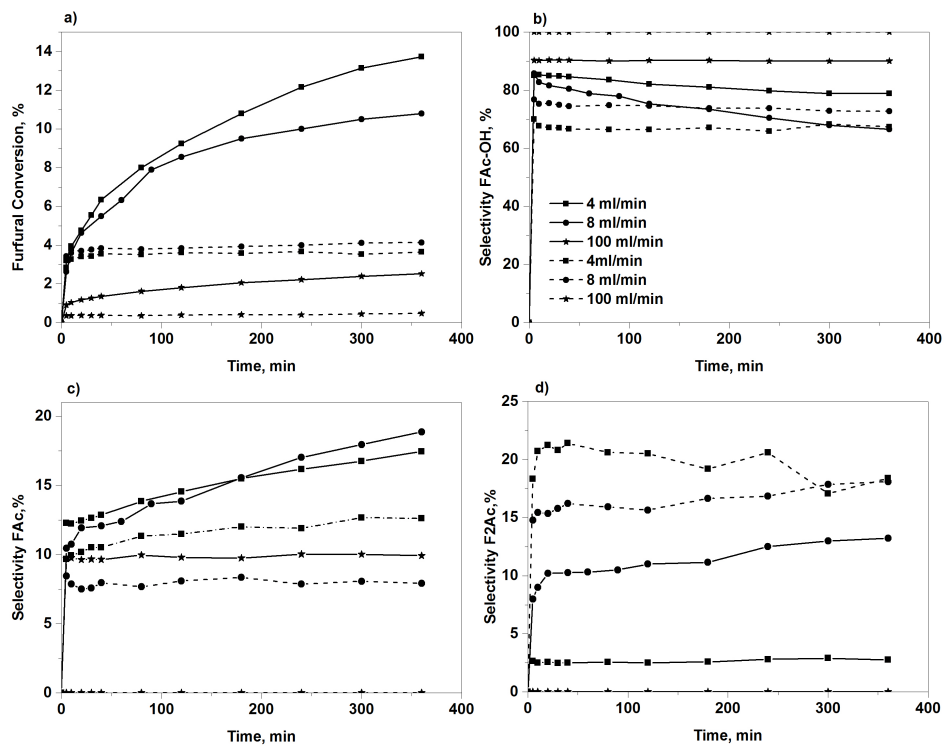


Fig. 11 The dependence of conversion and selectivity for mixed oxides synthesis at different flow rate of addition of cations solution of co-precipitation (solid line) and their rehydrated form (dash line)

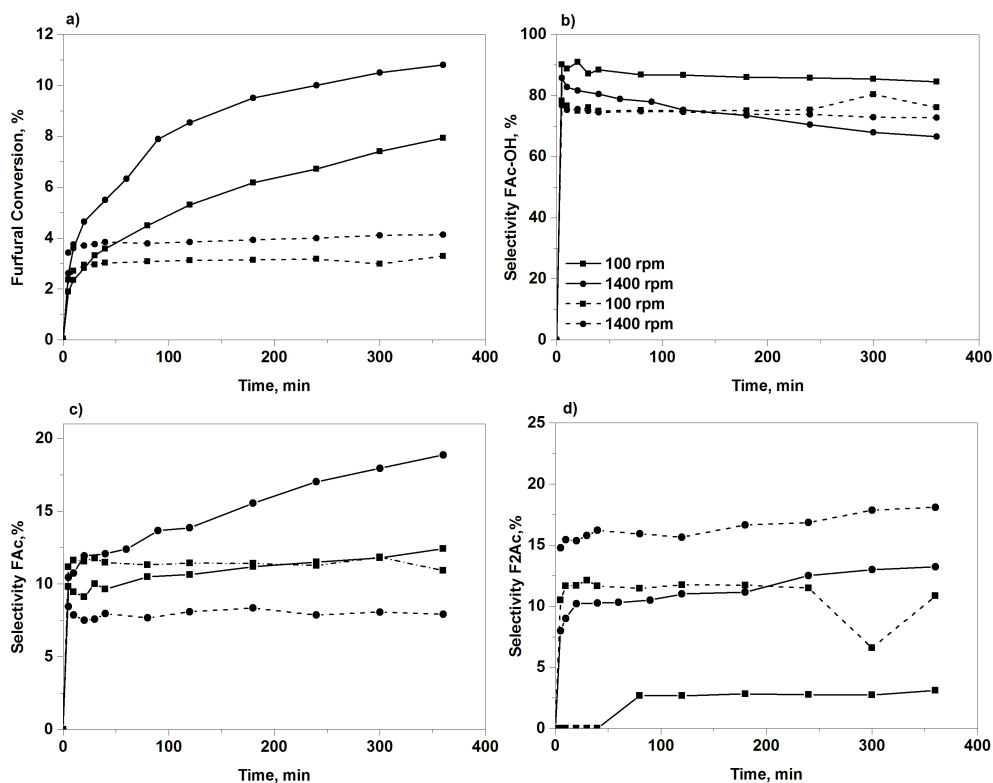


Fig. 12 The dependence of conversion and selectivity for mixed oxides synthesis at different intensity of stirring during co-precipitation (solid line) and their rehydrated form (dash line)

reaction processed in several consequent steps (Scheme 1); the flow rate of cations solution having an evident effect on the conversion.

The cations added at a flow rate of 4 and 8 ml min⁻¹ led to nearly the same conversion of furfural: 13 % and 11 %, respectively. On the other hand, when the rate of nitrates was 100 ml min⁻¹ only 3 % conversion was achieved. It could be seen, that for 4 and 8 ml min⁻¹, the F2Ac was formed; when the nitrates being added faster (100 ml min⁻¹) catalysts were not active as indicated by a low selectivity of F2Ac (maximally 1 %).

A lower conversion with rehydrated Zn-Al mixed oxides was achieved in comparison with Zn-Al mixed oxides. The reason could be that rehydrated mixed oxides contained more water, which might deactivate the centers in the mixed oxides. The conversion of Zn-Al was 4, 3, and 0 for 4, 8, and 100 ml min⁻¹, respectively.

The aldol condensation catalyzed by the mixed oxides prepared by hydrotalcite synthesis at different stirring rates was studied at a very end (Fig. 12). It was found, that when the reaction mixture had been stirred at 1000 rpm, the Zn-Al mixed oxides achieved the furfural conversion of 11%, whereas stirring at only 100 rpm led to a conversion of 8 % only. When the catalysts were rehydrated, the furfural conversion dropped down to 5 %.

Conclusion

The hydrotalcites at different co-precipitation conditions, such as pH, the concentration of ions, temperature throughout co-precipitation, and the intensity of stirring, were successfully synthesized. As found out, there was no clear and notable dependence between the conditions of synthesis and the crystallite size or specific surface area, except the temperature effect during the co-precipitation process. The hydrotalcites can be synthesized at conditions, such as properly low temperature, low stirring intensity, as well as a low concentration of nitrates at high flow rates of nitrates, making the synthesis faster.

Other subjects of studies, the mixed oxides, were formed by calcination of hydrotalcites, when selected (mixed) oxides were also rehydrated. Finally, both forms of these oxides were tested as catalysts for aldol condensation having ascertained that rehydration lowered the conversion degree of furfural for all the rehydrated oxides tested.

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