Catalysis Today xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Comparative study of physico-chemical properties of laboratory and industrially prepared layered double hydroxides and their behavior in aldol condensation of furfural and acetone

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ARTICLE INFO

Article history:
Received 24 October 2013
Received in revised form 2 March 2014
Accepted 5 March 2014
Available online xxx

Keywords:
Aldol condensation
Layered double hydroxides
Hydrotalcites
Furfural
Acetone

ABSTRACT

In this article, properties of laboratory and industrially prepared Mg–Al layered double hydroxides (LDH) with Mg:Al molar ratios varied in the range from 2 to 4 were compared. Physico-chemical properties of the studied materials were investigated with XRD, SEM, N_2 physisorption, TGA and CO_2-TPD methods. Catalytic behavior of the LDH samples was examined in the liquid phase aldol condensation of furfural and acetone at 20 and 60 °C. It was found that LDH from the small-scale preparation have different physico-chemical characteristics than the LDH materials originating from the large-scale (industrial) preparation which is also reflected in their catalytic behavior. As-synthesized laboratory LDH catalysts are phase-pure crystalline samples with hydrotalcite structure while the industrial materials also possess MgO as admixture. The laboratory samples possess larger BET surface area and mesopore volume in comparison with the industrially prepared ones. Despite the similarity in basic properties of the studied materials, the samples with molar ratio Mg:Al = 3 in both groups of LDH using different method of preparation possess the best activity in aldol condensation. Generally, the calcined laboratory samples are more active than the industrial materials in the reaction. This is explained by the better textural properties of the former ones and their susceptibility to in-situ reconstruction in the presence of water formed during the reaction.

1. Introduction

Layered double hydroxides (LDH) are formed by substitution of atoms of the matrix crystalline framework on atoms of elements with different valence. Among them, hydrotalcites (HTC) are mostly known, which possess a brucite-like $[Mg(OH)_2]$ network wherein isomorphous substitution of Mg^{2+} ion by a trivalent cation M^{3+} occurs and the excess positive charge is compensated by anions which are located in the interlayer along with water molecules. Consequently, they exhibit basic properties and could be used in a number of reactions of organic synthesis, including C–C bond formation, isomerization, cyclization, etc. [1–4].

Synthesis of fine chemicals from biomass by heterogeneously catalyzed reactions is a recent topic of great importance particularly in the view of the finite reserves of fossil resources and the connected adverse environmental impacts of the use of these non-renewable resources [5,6]. Among them, aldol condensation is an important reaction as it allows obtaining compounds with larger number of C atoms starting from simple organic molecules [1,7,8] that are typical intermediates in biomass processing. Moreover, it makes possible the evaluation of the catalysts from the viewpoint of the peculiarities of their physicochemical characteristics. As a result, the attention is focused on the search of efficient catalysts for aldol condensation due to the prospect of creating new technologies for the synthesis of fine chemicals, pharmaceuticals, plasticizers and fragrances from renewable chemicals [3,9,10]. Until now the industrial aldol condensation technologies rely on the use of NaOH as a catalyst, which results in high operation costs and serious environmental problems [11,12]. Hence, the development of basic heterogeneous catalysts, for example HTC, for this field is essential. A lot of publications accessible in open literature deal with different methods of preparation of HTC materials on laboratory scale [13–16], as well as with study of their physico-chemical and catalytic properties [17,18]. Nevertheless,

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http://dx.doi.org/10.1016/j.cattod.2014.03.010
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an objective assessment of the prospects of a new technology is hardly possible without estimation of the possibility to move from the laboratory synthesis of catalysts to the large-scale industrial preparation. However, publications on comparing the properties of laboratory and industrially prepared HTC samples in aldol condensation are missing. Therefore, the main objective of the present study is to provide information about differences between laboratory and industrially prepared hydrotalcites with respect to their physico-chemical and catalytic properties. Both groups of the materials were characterized by a number of methods (XRD, N2 physisorption, ICP, TGA, CO_2-TPD and SEM). Their catalytic properties were compared in aldol condensation of furfural and acetone which was chosen as a commonly used test reaction for evaluating basic properties of solids.

2. Experimental

2.1. Preparation of the samples

2.1.1. Preparation of catalysts precursor

Industrially prepared Mg–Al hydrotalcites with Mg/Al molar ratio ranging from 2:1 to 4:1 were provided by Eurosupport Manufacturing Czechia (ESMC) as dried samples at temperature 150 °C. They were denoted HTC Mg/Al molar ratio-I; e.g. HTC 3:1-I denotes industrially prepared hydrotalcite sample having Mg/Al molar ratio equal approximately to 3:1.

Laboratory prepared Mg–Al hydrotalcites with Mg/Al the same molar ratio ranging from 2:1 to 4:1 were synthesized by co-precipitation at constant pH value. They were denoted HTC Mg/Al molar ratio-L; e.g. HTC 3:1-L denotes laboratory prepared hydrotalcite sample having Mg/Al molar ratio equal approximately to 3:1. The preparation procedure involves mixing of an aqueous solution of magnesium nitrate $Mg(NO_3)_2{\cdot}6H_2O$, p.a. (Lach-Ner) and aluminum nitrate $Al(NO_3)_2{\cdot}9H_2O$, p.a. (Lach-Ner), solution A, and a basic solution of potassium carbonate K_2CO_3, p.a. (Lachema) and potassium hydroxide KOH, p.a. (Lach-Ner), solution B. Solution A contained always the same concentration of $Mg(NO_3)_2$ 8.2 wt% and the appropriate amount of $Al(NO_3)_3$ in order to obtain hydrotalcite with the desired Mg/Al molar ratio. Solution B used as precipitation agent was prepared by dissolving relevant amount of K_2CO_3 and KOH in order to obtain content 5.9 wt% of K_2CO_3 and 14.4 wt% of KOH.

In the synthesis procedure, 500 ml of demineralized water was placed in a 4000 ml baker and heated to temperature 60 °C. This temperature was stayed constant for the duration of the precipitation procedure. Solution A was dropped via membrane pump (STEPDOS FEM 08) into the baker under vigorous stirring. Flow rate of solution A was 10 ml per minute. At the same time, solution B was added into the baker via membrane pump (KNF Liquidport NF 100 FT.18RC) connected with pH controller (OMEGA INFCPH PHCH-37) which set up flow rate of solution B for constant pH value 9.5 maintaining.

After that, the obtained suspension was stirred at 60 °C for 1 h. Then the solid LDH was separated by filtration, washed with demineralized water and dried at temperature 60 °C for 12 h.

2.1.2. Catalyst activation

The following calcination procedure was applied to transform the as supplied LDH materials into catalysts. As-prepared LDH materials were calcined at 450 °C in air and mixed Mg–Al oxide catalysts were obtained. The temperature during calcination was raised at the rate of 5 °C/min to reach 450 °C and maintained for 16 h. The calcined mixed oxides were used as catalysts in aldol condensation reaction directly.

2.2. Physico-chemical methods

The crystallographic structures of dried LDH catalysts were determined by X-ray powder diffraction using a Philips MPD 1880, working with the Cu-K_α line ($\lambda = 0.154$ nm) in the 2Θ range of 5–70° at a scanning rate of 2Θ of 2.4°/min. The size and shape of hydrotalcite crystals were determined by scanning electron microscopy (Jeol, JSM-5500LV). The elemental composition was determined by ICP-OES equipment (HPST, Agilent 725). The textural properties of the catalysts (specific surface area and pore volume) were measured by nitrogen physisorption at 77 K using a Micromeritics TRISTAR 3000 surface area and porosity analyzer. Thermogravimetric analysis (TGA) of dried LDH catalysts were obtained using a TA Instruments TGA Discovery series operating at heating ramp 10 °C/min from room temperature to 900 °C in flowing of nitrogen (20 ml/min, Linde 5.0). Approximately 15 mg of sample was heated in an open alumina crucible.

Temperature programmed desorption of carbon dioxide as probe molecule (TPD-CO_2) was carried out on AutoChem equipped with a TPD detector and mass spectrometry using quadrupole spectrometer (MS OmniStar). Approximately 100 mg of catalyst (grain of 0.25–0.5 mm) was placed in quartz reactor. Before TPD experiments the catalysts were outgassed at 450 °C for 4 h in a flow of helium. Subsequently the catalysts were cooled down to 0 °C and treated with a CO_2 flow (99% purity) for 30 min. Weakly adsorbed CO_2 was removed by flushing with He at 0 °C for 30 min. The desorption of CO_2 was measured by heating the catalyst from 0 to 900 °C at a heating rate of 10 °C/min in He flow. The desorbed products were analyzed by mass spectrometry. The number of basic sites was calculated from the CO_2 peaks (the molecular ion, $m/z = 44$) with help of calibration using a known amount of CO_2 desorbed from $CaCO_3$ [19].

2.3. Reaction studies

The experiments were carried out in a 100 ml stirred batch reactor (a glass flask reactor) at temperatures 20 and 50 °C. Before the start of an experiment, 2 g of catalyst was mixed together with a stirred mixture of 39.5 g acetone and 6.5 g furfural (acetone/furfural molar ratio 10:1, dried with molecular sieve 3A, pre-heated to the desired reaction temperature) and kept at this temperature for 6 h under intensive stirring. Before performing the series of experiments, it has been established that under the chosen reaction conditions the reaction is limited neither by external nor internal mass transfer by changing the stirring rate and catalyst particle size. As synthesized and calcined catalyst agglomerates with particle size less than 350 μm were used in the experiments. Samples were withdrawn from the reactor during the experiment (one sample per 1 h), filtered, and analyzed by Agilent 7890A gas chromatograph equipped with a flame ionization detector (FID), using a HP 5 capillary column (30 m/0.32 mm ID/0.25 μm). Reaction pathway of aldol condensation of furfural with acetone is shown in Scheme 1.

Catalytic results of aldol condensation of furfural and acetone have been described by conversion and selectivity parameters that have been calculated as follows:

$$\text{reactant conversion}\,(t)\,(\text{mol\%}) = 100 \times \frac{(\text{reactant}_{t=0} - \text{reactant}_t)}{\text{reactant}_{t=0}};$$

$$\frac{\text{selectivity to product } i = (\text{mole of reactant converted to product } i)}{(\text{total number of mole of reactant converted})}.$$

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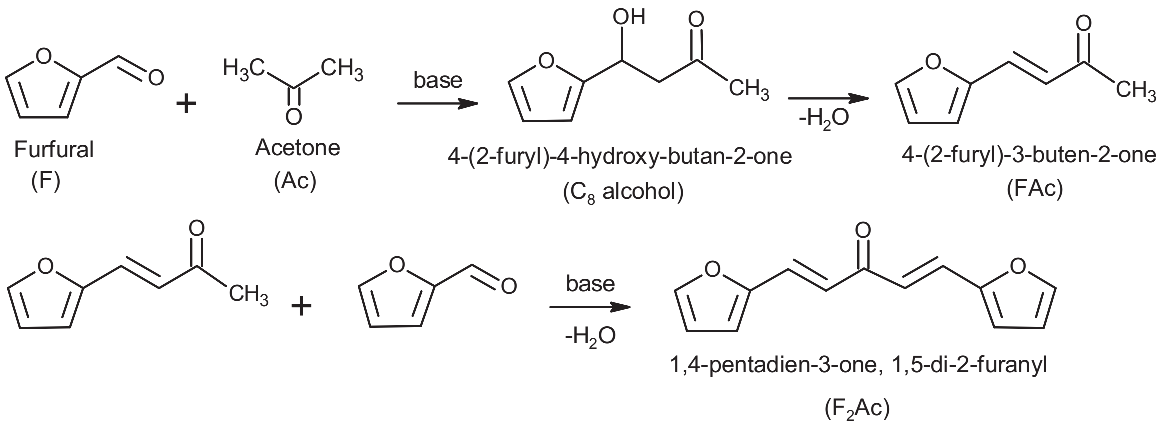

Scheme 1. Mechanism of the condensation reactions of furfural and acetone.

The carbon balance calculated as the carbon atoms detected in each sample (C_3, C_5, C_8 and C_{13}) divided by the initial carbon atoms (C_3 and C_5 fed) has been preserved during all experiments:

$$\mathrm{C\,balance\,\%} = \frac{(3\ \ \mathrm{mol\,C3} + 5\ \ \mathrm{mol\,C5} + 8\ \ \mathrm{mol\,C8} + 13\ \ \mathrm{mol\,C13})}{(3\ \ \mathrm{mol\,C3}_{t=0} + 5\ \ \mathrm{mol\,C5}_{t=0})}$$

3. Results and discussion

3.1. XRD study

Fig. 1 depicts XRD patterns of the samples under study. Three laboratory prepared samples, HTC 2:1-L, HTC 3:1-L and HTC 4:1-L (Fig. 1A), possess the typical diffractograms of hydrotalcite-like materials. The intensive peaks at $2\theta \approx 11^\circ$, 23° and 34° correspond to the (0 0 3), (0 0 6) and (0 0 9) planes [14,20], indicating a well-formed crystalline layered structure. A small shift of these characteristic peaks of HTC structure toward low-angle region is observed with the increasing Mg/Al molar ratio. This shift may suggest the basal spacing expansion due to e.g. a difference in nature of the intercalated anions which are presented in the interlayer space [21]. Unlike the laboratory samples, the XRD patterns of the materials prepared in an industrial large-scale basis indicate presence of more than one crystalline phase. Along with the presence of XRD peaks corresponding to the HTC structure, there are also reflexes from magnesium oxide and magnesium hydroxide. It may be assumed that in the course of large scale preparation an incomplete interaction of the initial reactants has occurred. As a result the content of the desired HTC structure decreased at the expense of the simultaneous formation of MgO and $Mg(OH)_2$ admixture phases. It is clearly seen that the intensity of the characteristic peaks of the HTC structure is lower in the industrial samples in comparison with for the laboratory ones. Among the large-scale prepared materials, the intensity of the peaks attributed to both HTC and MgO phases is the highest for the HTC 2:1-I sample while the intensity of the peaks of $Mg(OH)_2$ phase is the highest for HTC 4:1-I and HTC 3:1-I samples.

The XRD patterns of the calcined samples (Fig. 1B) exhibit peaks at $2\theta \approx 37^\circ$, 43° and 62° which correspond to diffraction by the (1 1 1), (2 0 0) and (2 2 0) planes of periclase MgO phase [14]. The change of diffractograms reveals that the layered HTC structure was completely transformed after the heat treatment of the samples. It is believed that after the calcination the aluminium compounds should be well-dispersed in the MgO phase or should form a separate amorphous phase [22]. It is also seen that peaks reflections of MgO structure are higher and sharper for

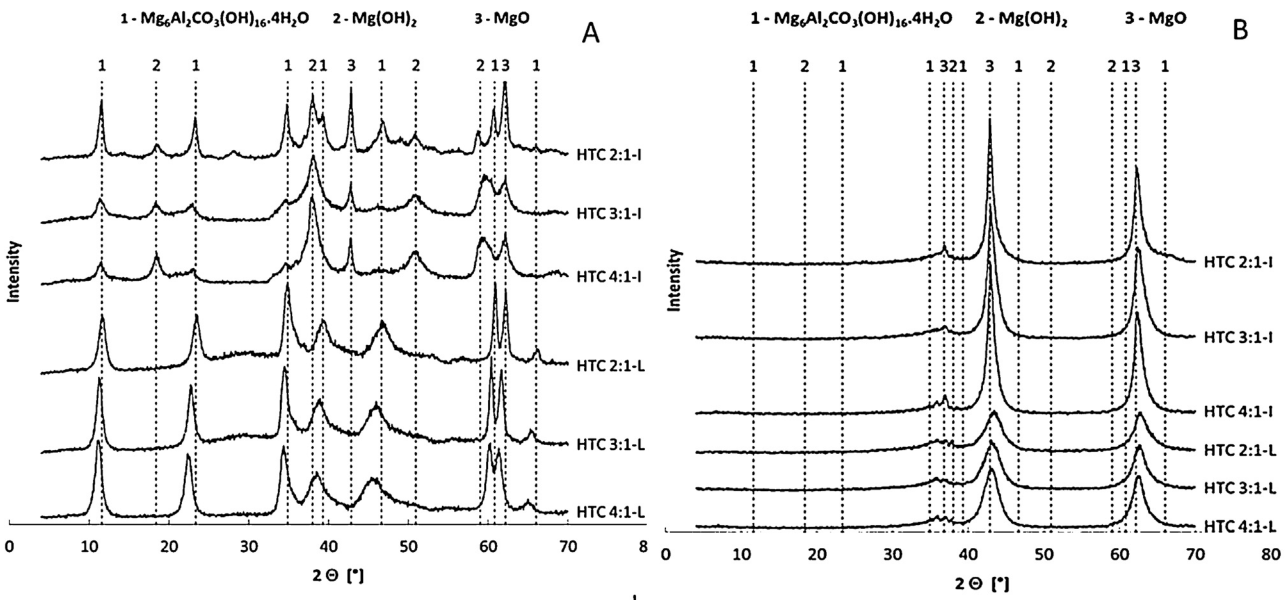

Fig. 1. XRD patterns of the laboratory and industrially prepared samples with different Mg/Al molar ratio. (A) Raw materials, (B) calcined materials.

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Table 1
Chemical composition of the laboratory and industrially prepared samples and crystallite size of the calcined materials.

Parameter/sample	Unit	HTC 2:1-I	HTC 3:1-I	HTC 4:1-I	HTC 2:1-L	HTC 3:1-L	HTC 4:1-L
Mg	wt%	11.3	13.2	14.9	10.5	14.8	11.8
Al	wt%	5.6	4.5	4.0	5.7	5.4	3.2
Si	wt%	0.1	0.06	0.05	0.04	0.04	<0.02
Ca	wt%	0.12	0.08	0.11	0.02	0.02	0.01
Fe	wt%	0.05	0.03	<0.02	<0.02	<0.02	<0.02
K	wt%	<0.02	<0.02	<0.02	0.03	0.02	0.08
Mg:Al	mol/mol	2.24	3.28	4.14	2.06	3.03	4.09
L_{200}	nm	17.1	15.5	21.4	7.1	7.1	7.1

the calcined industrially prepared samples in comparison with the laboratory ones. The crystallite size of the mixed oxides was estimated from the plane $(2\,0\,0)$ $(2\theta \approx 43^{\circ})$ using the Debye–Scherrer equation [23], and the calculated values are presented in Table 1.

3.2. SEM

Fig. 2 shows SEM images of the prepared samples. It is seen that the large-scale prepared samples represent large agglomerates of 10–15 μm, which consist of tightly compacted sheets of a layered

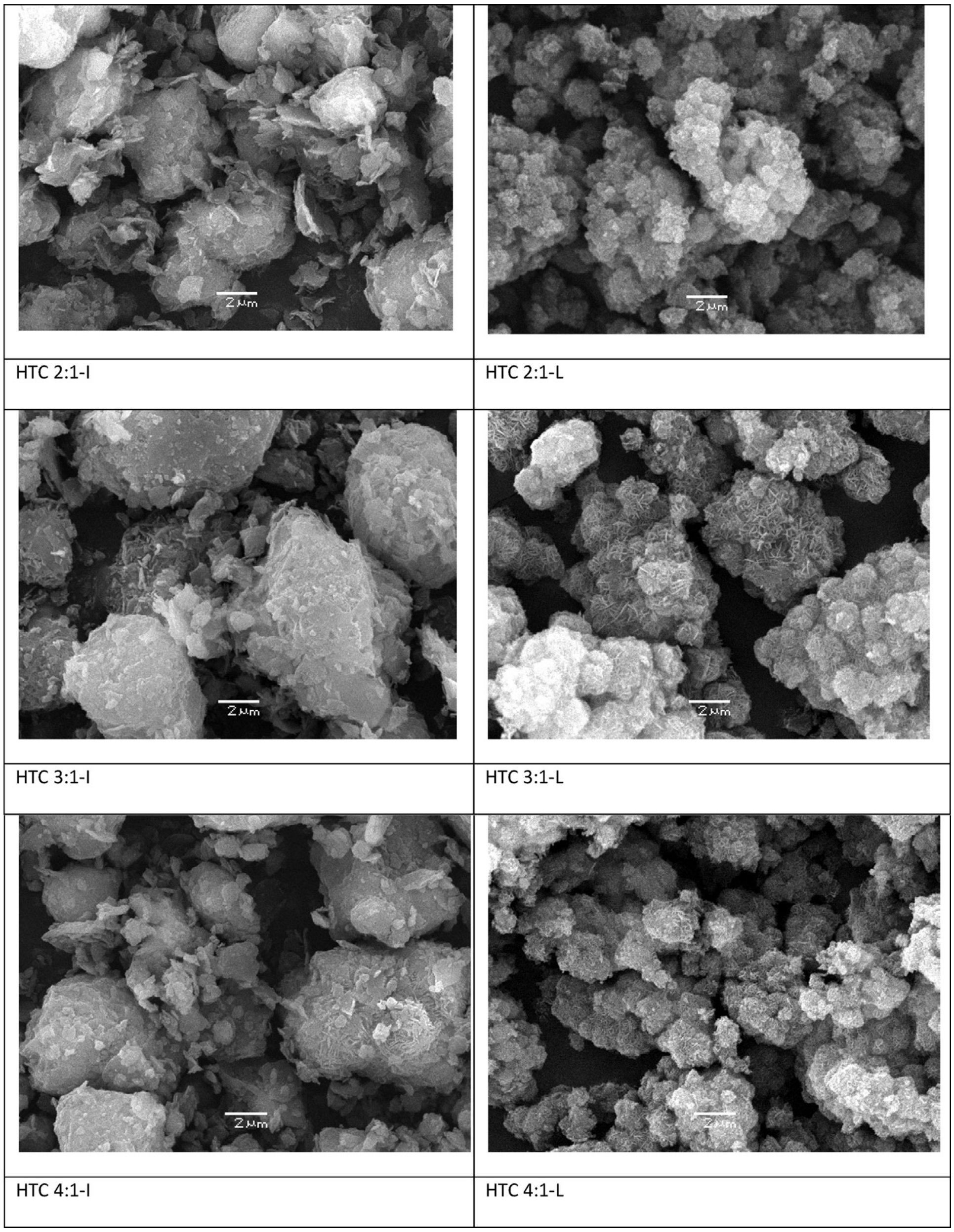
HTC 2:1-I
HTC 2:1-L
HTC 3:1-I
HTC 3:1-L
HTC 4:1-I
HTC 4:1-L

Fig. 2. SEM images of laboratory and large-scale prepared HTC samples with different Mg:Al molar ratio.

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Table 2
Textural properties of laboratory and industrially prepared LDH samples.

Sample	BET surface area (m^2/g)	Pore volume* (cm^3/g)	Pore volume$_{1-4\,nm}$ (cm^3/g)	Pore volume$_{4-10\,nm}$ (cm^3/g)	Pore volume$_{10-50\,nm}$ (cm^3/g)
HTC 2:1-I	167	0.41	0.09	0.16	0.15
HTC 3:1-I	164	0.34	0.11	0.13	0.08
HTC 4:1-I	159	0.33	0.1	0.14	0.07
HTC 2:1-L	247	1.18	0.03	0.07	0.96
HTC 3:1-L	213	1.08	0.02	0.10	0.91
HTC 4:1-L	200	0.96	0.05	0.10	0.74

* BJH method.

material. At the same time, small particles of micron size also possessing a layered structure can be determined. These are likely to be fragments of the large agglomerates. Laboratory samples also represent large agglomerates up to 10 μm, which consist of small shapeless particles of 1–2 μm in size. A more detailed analysis of the images of the laboratory prepared samples reveals that these small particles possess a well-developed layered structure which is characteristic of the LDH materials [24].

3.3. Chemical analysis

Chemical composition of all the materials in the as-dried form was determined by the ICP method. Results presented in Table 1 show that Mg/Al molar ratio in the samples is close to the claimed content of these elements. The main impurities in the industrially prepared samples include small amounts of Fe, Ca and Si, while the laboratory samples occasionally contain a detectable amount of potassium.

3.4. Textural properties

Table 2 presents data on textural properties of the samples. The obtained results show that in the two groups of differently prepared samples both BET specific surface area (BET SSA) and the total pore volume increase as Mg/Al molar ratio decreases. BET SSA for the laboratory samples increases from 200 m^2/g for HTC 4:1-L to 247 m^2/g for HTC 2:1-L while the total pore volume increases in the same direction from 0.89 cm^3/g to 1.06 cm^3/g. BET SSA and the total pore volume of the industrially prepared samples are lower being in the range of 159–167 m^2/g and 0.31–0.4 cm^3/g, respectively. The pore size distribution provides additional information about the difference in the textural properties of the two groups of

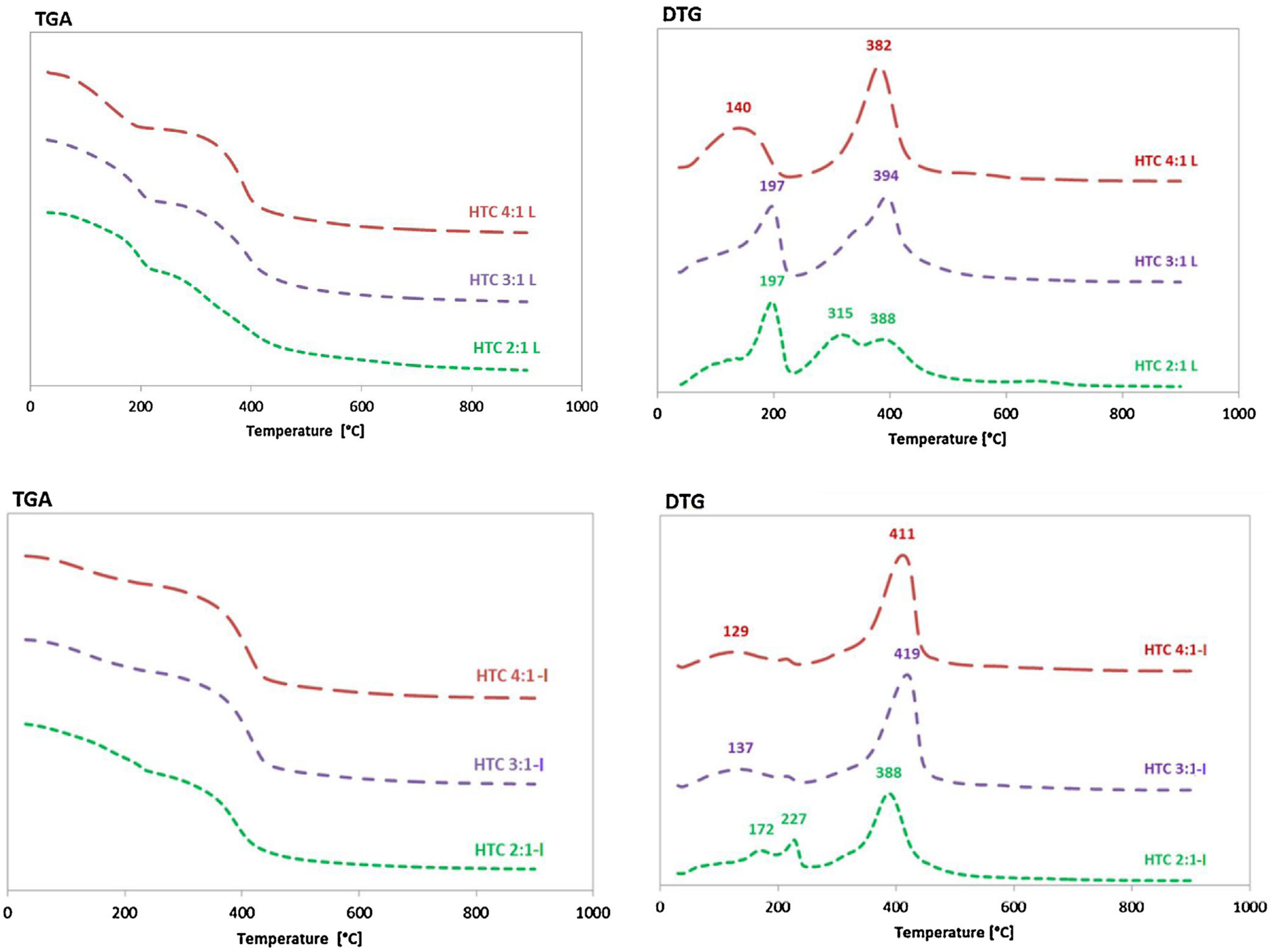

Fig. 3. TGA/DTG curves of the fresh laboratory and industrially prepared LDH catalysts.

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Table 3
Weight loss at different stages of heat treatment of the laboratory and industrially prepared LDH samples.

Sample	Temperature range (°C)	Maximum of peak (°C)	Weight loss (%)
HTC 2:1-L	20–220	116, 193	16.5
	220–500	309, 379	25.1
	≥500	650	1.9
HTC 3:1-L	20–220	106, 193	17.3
	220–500	335, 390	26.3
	≥500	–	0
HTC 4:1-L	20–220	130	15.7
	220–500	375	25.7
	≥500	530	2.2
HTC 2:1-I	20–250	160, 219	11.8
	250–500	382	21.5
	≥500	–	0
HTC 3:1-I	20–240	125	7.5
	240–500	412	24.1
	≥500	555	1.8
HTC 4:1-I	20–240	117	6.7
	240–500	406	24.3
	≥500	563	1.7

HTC samples (Table 2). For the industrial materials the pore size distribution in the range of 1–50 nm is quite uniform and amounts to 0.07–0.16 cm^3/g. Apparently, a relatively large contribution of the small pores of 1–4 nm in the industrially prepared samples could be a result of close packing of the layers which make up the large agglomerates, as evidenced by the SEM images (Fig. 2–left column). In contrast, most of the pores in the laboratory samples are in the range of 10–50 nm, which is a consequence of the specific morphology of the hydrotalcite materials (Fig. 2—right column) [24].

3.5. Thermal decomposition of LDH materials

The process of the transformation of a hydrotalcite structure into mixed oxides was investigated by thermal analysis of the samples. TGA/DTG profiles of decomposition of the laboratory and industrially prepared materials are presented in Fig. 3. All of the studied samples show three general decomposition steps that are accompanied by weight loss. The first step occurs at 50–200 °C and is ascribed to the loss of physically adsorbed and interlayer water molecules [20,24]. The second step takes place in the range of 200–500 °C and corresponds to the loss of layer OH^- groups and decomposition of the interlayer carbonates [24]. Due to this stage a transformation of the layered structure to the mixed oxide takes place [25]. At temperatures above 500 °C, the DTG curves of several samples contain an additional peak which could be possibly attributed to removal of the residual interlayer species.

Table 3 summarizes the weight losses observed at each step of the thermal treatment of LDH samples. The amount of desorbed water is higher for the laboratory samples in comparison with the industrially prepared ones, 15.7–17.3% and 6.7–11.8%, respectively. The observed difference in water amount may be attributed to different HTC content in the samples what is proved by XRD data (Fig. 1A). The asymmetrical shape of the curve at this stage observed for several samples could be explained by the co-existence of two modes of the water adsorption, namely loosely surface-adsorbed and bound interlayer water. The weight loss at the second step amounts to 25.1–26.3% for the laboratory samples and 21.5–24.3% for the industrial samples. It is seen that in the case of HTC 2:1-L, and to a lesser degree, HTC 3:1-L, the signal in the range of $T = 300–400$ °C is splitted to two different peaks. According to [14], the loss of OH^- groups is observed at lower temperatures than CO_2 removal. So, the observed splitting of the signal at the second step may be attributed to the dehydroxylation of the interlayer space followed by decarbonation. On the other hand, the thermal decomposition of the industrially prepared samples (Fig. 3) as well as of the HTC 4:1-L sample exhibits only one dominant peak at the temperature in the range of 375–412 °C. When comparing the obtained results of the thermal analysis it may be concluded that the difference between the samples originates not only from the amount of the desorbed species but also from their nature.

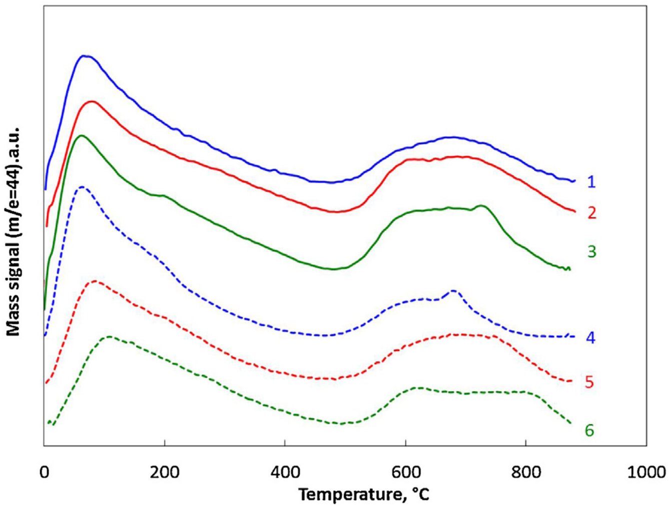

Fig. 4. CO_2-TPD spectra of laboratory (HTC 2:1-L (1), HTC 3:1-L (2), HTC 4:1-L (3)) and industrially (HTC 2:1-I (4), HTC 3:1-I (5), HTC 4:1-I (6)) prepared samples.

3.6. CO_2-TPD

The results of the investigation of basicity of the LDH samples by means of CO_2-TPD method are presented in Fig. 4 and Table 4. CO_2-TPD spectra of the samples indicate presence of at least two types of basic sites located in low temperature ($T = 20–500$ °C) and high temperature ($T \geq 500$ °C) regions. It is known that the basic sites can be classified according to their different strengths (i.e. different

Table 4
Concentration of basic sites in the samples.

Sample	CBS* 20–485 °C [μmol/CO_2/g_{cat}]
HTC 2:1-L	640
HTC 3:1-L	642
HTC 4:1-L	753
HTC 2:1-I	718
HTC 3:1-I	549
HTC 4:1-I	547

* CBS—concentration of basic sites.

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carbon dioxide desorption temperature). In accordance with this dependence peaks located in the two above-mentioned temperature regions indicate presence of weak/moderate and strong basic sites, respectively. However, as pointed out in [26], information obtained from CO_2 desorbed at temperatures above the calcination temperature of the solids should be carefully considered since structural transformations could occur on the samples. Since the samples of the present work were calcined at $T = 450\,^{\circ}C$, the high temperature peak at $T \geq 500\,^{\circ}C$ in the CO_2-TPD curve was excluded from the discussion of the obtained results. CO_2-TPD spectra presented in Fig. 4 show that the shape of all the low-temperature peaks in the range of 25–485 °C is essentially the same for different samples and does not reveal any significant dependence neither on the preparation method nor on the chemical composition of the samples. Table 4 gives total amount of desorbed CO_2 detected in TPD-CO_2 profiles of Mg–Al mixed oxides in the range of 25–485 °C. The obtained results show that the highest concentration of basic sites in the laboratory samples is observed for HTC 4:1-L (753 μmol CO_2/g), while this value for HTC 2:1-L and HTC 3:1-L is approximately the same and amounts to 640–642 μmol CO_2/g. For industrially prepared samples a reverse tendency is observed. The highest concentration of basic sites is observed for HTC 2:1-I with the highest Al content (718 μmol/CO_2/g), while for HTC 3:1-I and HTC 4:1-I this value is 547–549 (μmol CO_2/g).

3.7. Catalytic experiments

Fig. 5 depicts catalytic behavior of the calcined laboratory and industrially prepared samples. Experiments at two different reaction temperatures, $T = 20\,^{\circ}C$ and 50 °C, show that all the samples possess good activity in aldol condensation of furfural and acetone (Fig. 5A and B). Already after 1 h of the experiment furfural conversion reaches 10–17% at $T = 20\,^{\circ}C$ and 40–83% at $T = 50\,^{\circ}C$. After 6 h of the reaction furfural conversion is 17–36% and 79–100% at $T = 20^{\circ}$ C and $T = 50^{\circ}$ C, respectively. As a result of reaction between furfural and acetone the formation of C_8 alcohol, FAc and F_2Ac takes place, which is in full agreement with the commonly accepted scheme of aldol condensation of F and Ac over basic catalysts (see Scheme 1). The selectivity toward C_8 alcohol (Fig. 5C and D), FAc (Fig. 5E and F) and F_2Ac (Fig. 5G and H) shows a dependence on both furfural conversion and the type of the used catalyst. The compounds formed due to self-condensation of acetone to diacetone alcohol with its further transformation are also observed among the reaction products, but here we exclude them from the consideration as their overall concentration among all reaction products does not exceed 8 wt% and furfural is not involved in their formation.

A steep increase of FAc selectivity at high F conversion (>80%) is observed at $T_{reac.} = 50\,^{\circ}C$ (Fig. 5F). The comparison of FAc and Fac-OH selectivities indicates that with the increase of the TOS the ability of the catalyst to dehydrate the intermediate alcohol is enhanced. It can assumed that consecutive changes in the catalytic properties of the catalyst are the result of the partial reconstruction of HTC structure due to the interaction of the catalyst with water released during the reaction, as discussed below. Fig. 5 shows that at 50 °C the overall selectivity to (FAc + FAc-OH) decreases gradually with the increasing TOS, while the selectivity to F_2Ac increases showing an almost linear dependency on the F conversion.

In both groups of HTC catalysts, i.e. laboratory and industrially prepared HTC catalysts, the samples with molar ratio Mg:Al = 3:1 are the most active in aldol condensation. However, there is not any obvious dependence of the catalytic behavior of the samples on their chemical composition. For the laboratory prepared samples the conversion of furfural decreases in the order: HTC 3:1-L > HTC 2:1-L > HTC 4:1-L, whereas for the industrially prepared samples it decreases in a different order: HTC 3:1-I > HTC 4:1-I > HTC 2:1-I. Nevertheless, Fig. 5 shows that laboratory samples are clearly more active in furfural conversion than the industrially prepared ones. To explain this result it is necessary to take into account in addition to chemical composition also the collected data on the physico-chemical characterization of the samples.

The XRD patterns of the as-prepared dried laboratory samples show the characteristic peaks corresponding to HTC structure. After calcination this layered material is completely transformed into highly disordered structure of periclase (MgO) as proved by XRD. According to N_2 physisorption this disordered mixed oxide, independently on chemical composition, possesses high degree of mesoporosity. Contrary to that, the industrially prepared samples before calcination consist of a mixture of at least two crystalline phases, HTC and MgO, but after calcination the XRD patterns of these materials contain only peaks characteristic for highly-crystalline MgO phase which is made of large crystals (Table 1). As a consequence, these materials possess small mesopore volume, as proved by N_2 adsorption measurements (Table 2). Apparently, the small dimensions of the particles and high mesopores volume are very favorable for easy access of reactant molecules to the active sites of the disordered calcined LDH, i.e. the mixed oxide. Indeed, the improved textural properties of the laboratory samples show good correlation with the high activity of these samples in aldol condensation. So, generation of transport pores with dimensions ≥4 nm formed during the calcination process ensures improved transport of both reactants and reaction products, which is essential for preparing highly active catalysts. Despite this consideration, there is a disagreement between the textural characteristics of the prepared materials and their catalytic properties. Fig. 5 shows that activity of HTC 3:1-I sample is almost similar to that of HTC 4:1-L sample. At the same time, the textural data presented in Table 2 prove that BET SSA and mesopores volume is significantly higher for HTC 4:1-L when compared with HTC 3:1-I. It means that other factor(s) that affect the catalytic behavior of the studied catalysts need to be taken into account.

Among these factors basicity of the materials is an obvious parameter that might affect significantly the catalytic behavior of HTC materials in aldol condensation. It is known [27] that calcined Mg–Al hydrotalcites can contain basic sites with p*K*a values up to 16.5. These sites act, in fact, as weak Lewis acid/strong Lewis base catalysts due to the presence of O^{2-} basic sites. Indeed, Fig. 4 and Table 4 confirm the presence of basic sites in all the studied samples. Their concentration measured by CO_2-TPD is in the range of 547–753 μmol/g. Additionally, it seems that their strength is also approximately the same, as the temperature at the CO_2 desorption peak maximum as well as the shape of the signals are approximately the same and show neither dependence on the chemical composition of the samples nor the method of their preparation. By comparing the obtained CO_2-TPD data and catalytic results it is hardly possible to introduce a definite correlation between the basic properties of the mixed oxides and their behavior in aldol condensation. It may be concluded that in this case basicity of the samples is an important but not a determining factor which could unambiguously explain the obtained experimental results.

Investigating influence of basic properties of HTC materials on their catalytic behavior in aldol condensation of furfural and acetone it is necessary to consider conformity of the interlayer distance in HTC materials with dimensions of reactant molecules. A distance between layers of HTC structure is 2.9 Å [28], and kinetic diameter of CO_2 is 3.9 Å [29]. Taking into account a linearity of CO_2 molecule it could be assumed that determination of basic sites in the interlayer space of HTC with CO_2-TPD is reasonable. However, molecular diameter of acetone is larger, 6.16 Å [30], and it is hardly possible that this molecule could interact with interlayer active sites. So, concentration of basic sites measured by CO_2-TPD should be higher than amount of active sites accessible to acetone molecules. Consequently, one should be careful in finding correlation between

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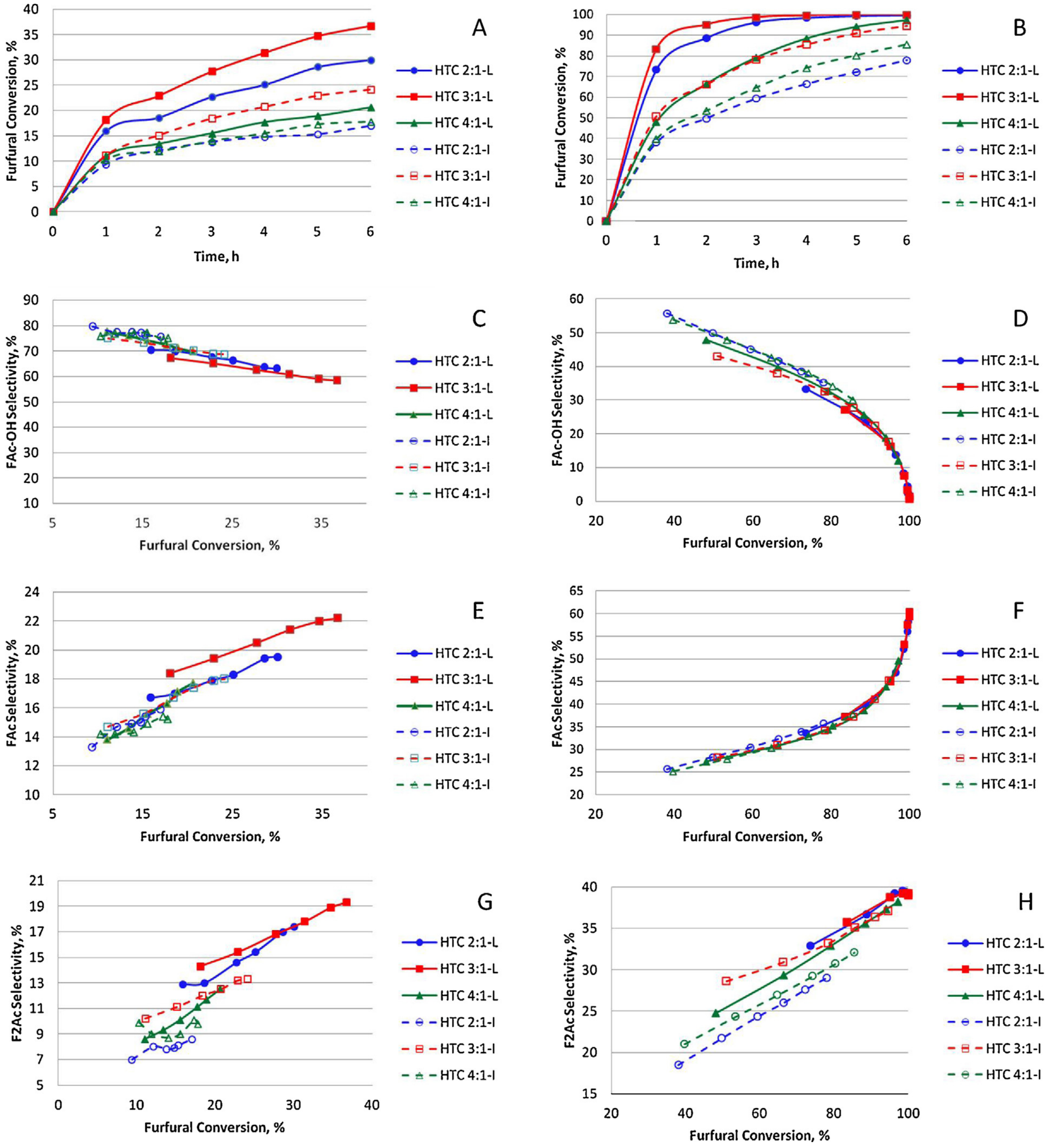

Fig. 5. Catalytic properties of calcined LDH samples at $T = 20\,^{\circ}C$ (left) and $T = 50\,^{\circ}C$ (right). (A) and (B) Furfural conversion in dependence on reaction time. C–H-products selectivity in dependence on furfural conversion ((C) and (D) FAc-OH, (E) and (F) FAc, (G) and (H) F_2Ac).

basic properties of HTC materials and their catalytic properties in reactions between large organic molecules.

In order to obtain additional information to explain the obtained catalytic results, we investigated the properties of the materials after the reaction. It is seen (Fig. 6) that the XRD patterns of the spent laboratory samples, HTC 2:1-L, HTC 2:1-L and HTC 4:1-L, contain very small peaks characteristic to the layered HTC structure. This observation indicates that during the reaction a partial reconstruction of the highly disordered mixed oxide to HTC phase takes place for these samples. As this can be achieved only by rehydration, the local reconstruction of the HTC structure is made possible only by water released during the reaction which reacts with the surface of the mixed oxide (as both raw materials were dried prior to the experiments using a molecular sieve). Simultaneously, the interaction of O^{2-} basic sites present in the calcined material with water formed due to aldol condensation results in the formation of OH^- Brønsted basic sites which provide higher activity to the reconstructed LDH materials in aldol condensation in comparison with the calcined ones [18,31]. Thus, the presented XRD results prove that samples HTC 2:1-L and HTC 3:1-L are the most susceptible catalytic materials to the presence of water formed during the reaction. As a result they exhibit higher catalytic activity in aldol condensation than the other studied materials.

At present it is difficult to reveal the underlying reason of the observed discrepancy. The reason could be that the aldol condensation reaction over HTC materials occurs with the participation of

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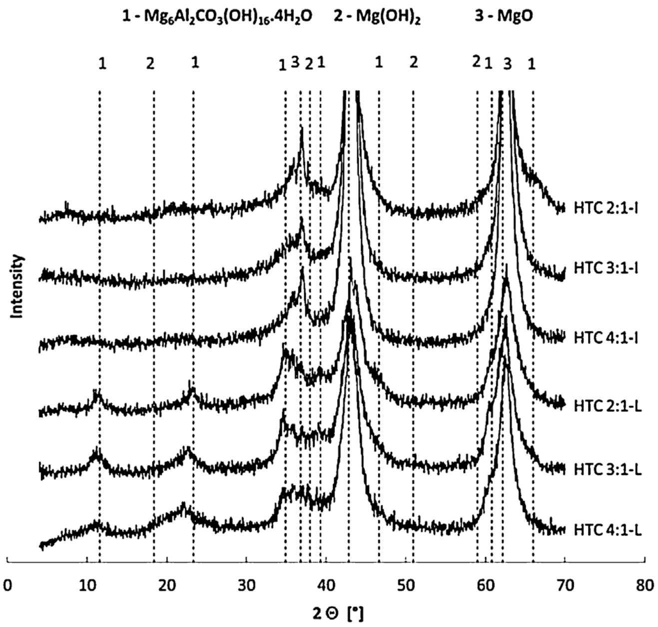

Fig. 6. XRD patterns of the laboratory and industrially prepared spent catalysts with different Mg:Al molar ratio.

those basic OH^- sites present in the reconstructed HTC which are readily accessible for the reactants, i.e. with the hydroxyl groups located at the edges of the platelets. Apparently, under the reaction conditions the water molecules interact only with the most accessible O^{2-} basic sites, i.e. with those located at the edges of the platelets. This limited interaction between these sites and water molecules may explain the observed low degree of reconstruction of the calcined material. As pointed out in [27], the amount of such accessible sites is connected with the presence of smaller and more irregular platelets which exhibit a higher proportion of the edges. Therefore, the possibility of formation of OH^- ions is determined by the degree of irregularity of the morphology of the materials. Hence, the samples 2:1-L and HTC 3:1-L should possess an increased degree of irregularity of the structure, which is indirectly confirmed by the low intensity of the reflections in the XRD patterns of the calcined laboratory prepared materials (Fig. 1). However, similar effect of the partial re-hydration is not observed for the industrially prepared samples, possibly due to decreased mesoporosity and larger crystal size of these materials, thus limiting the number of the sites available for interaction with water molecules. The laboratory sample HTC 4:1-L exhibits worse catalytic behavior than the other laboratory HTC sample which can be explained only by performing additional experiments. A detailed study of the re-hydration process in a dependence on the method of preparation of the samples and their chemical composition will be the subject of our forthcoming research.

4. Conclusions

Comparative study of properties of laboratory and industrially prepared Mg–Al LDH materials revealed that these two groups of solids differed in their physico-chemical characteristics. According to XRD study, as-synthesized laboratory samples represented phase-pure hydrotalcite structure that distinguished them from industrial samples which represented a mixture of hydrotalcite and MgO phases. Accordingly, the morphology and texture characteristics of the samples varied in the method of their preparation were also different. On the other hand, a study of the samples with CO_2-TPD showed that their basic properties did not reveal any dependence on the method of preparation. Besides, within each group of the materials no correlation between basic properties and chemical composition was observed. Catalytic experiments showed that all the samples exhibited good activity in aldol condensation of acetone and furfural. Catalysts with a molar ratio of 3:1 were the most active for both, laboratory and industrial, groups of the materials. Nevertheless, when comparing the samples of the same chemical composition, it was seen that laboratory samples possessed better properties in aldol condensation. The observed difference could be attributed to the increased mesoporosity of the laboratory samples. It was also proved by XRD method that in reaction conditions the calcined laboratory materials showed an increased susceptibility to reconstruction of mixed oxide phase back to hydrotalcite structure. As a consequence, this reconstruction resulted to a change in the structure of the active sites in the samples what could be also a reason of increased activity of the laboratory LDH materials. However, the received experimental results have showed that other factors that influence the catalytic properties of LDH materials may also exist, and elicitation of such factors is considered as a task for the forthcoming study.

Acknowledgments

Financial support from the Ministry of Industry and Trade of the Czech Republic (project FR-TI3/327) and Czech Science Foundation (P106/11/0773) is gratefully acknowledged. This publication was created in connection with the project Unipetrol research and education center Reg. CZ.1.05/2.1.00/03.0071, which is funded through the Operational Programme for Research and Innovation Development of the Structural Funds (specifically the European Regional Development Fund) and the state budget of the Czech Republic.

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