



# The occurrence of Cannizzaro reaction over Mg–Al hydrotalcites



Oleg Kikhtyanin<sup>a,\*</sup>, Estera Lesnik<sup>a</sup>, David Kubička<sup>b</sup>

<sup>a</sup> Unipetrol Centre of Research and Education, Block 2838, Záluží 1, 436 70 Litvínov, Czech Republic

<sup>b</sup> Technopark Kralupy VŠCHT Praha, University of Chemistry and Technology, Prague, Žitkova 7, 278 01 Kralupy nad Vltavou, Czech Republic

## ARTICLE INFO

### Article history:

Received 26 May 2016

Received in revised form 14 July 2016

Accepted 5 August 2016

Available online 5 August 2016

### Keywords:

Basic catalysis

Cannizzaro reaction

Mg–Al hydrotalcite

Mixed oxide rehydration

Aldol condensation

## ABSTRACT

Mg–Al mixed oxides and reconstructed hydrotalcites prepared from mixed oxides by rehydration attract much attention as solid basic catalysts for organic reactions, such as aldol condensation. Therefore, the understanding of parameters that govern their catalytic performance is of great importance. Cannizzaro reaction in the presence of mixed oxide and reconstructed HTC as basic catalysts was used as a model reaction to characterize both catalytic systems and to understand their behavior in aldol condensation. The performance of the samples was investigated in the conversion of aqueous furfural mixture using stirred batch reactor operating at  $T=50^{\circ}\text{C}$ . The properties of both initial samples and catalysts after reaction were studied by different physico-chemical methods, such as XRD, DRIFT and TGA. It was shown that both mixed oxide and reconstructed HTC possessed poor activity in the conversion of dried furfural proving the importance of water presence for the reaction to take place. Addition of water to the reaction mixture resulted in growth of the yield of both furfuryl alcohol and furoyl furoate as reaction products. Furoic acid was not identified by GC analysis, but the interaction of the acid with the basic sites of catalysts was confirmed by DRIFT and TGA analyses indicating that at optimum reaction conditions, most of the basic sites were involved in the formation of furoate species. The formation of the surface furoate species influenced the behavior of the basic catalysts in aldol condensation of furfural and acetone. It allows concluding that the occurrence of Cannizzaro reaction should be taken into account when considering the behavior of basic catalysts in organic reactions with furfural as a reactant.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

In recent years hydrotalcites (HTCs) have found numerous applications as adsorbents or ion exchangers, catalyst precursors or supports, etc. [1–4]. These materials represent a class of hydrated double hydroxides with a general formula  $[\text{M}^{2+}_n\text{M}^{3+}_m(\text{OH})_{2(n+m)}]^{m+}(\text{A}^{x-})_{m/x}\cdot y\text{H}_2\text{O}$ . The most commonly used Mg–Al HTCs consist of a brucite-like  $[\text{Mg}(\text{OH})_2]$  network wherein isomorphous substitution of  $\text{Mg}^{2+}$  ion by a trivalent  $\text{Al}^{3+}$  occurs and the excess positive charge of the framework is compensated by gallery anions which are located in the interlayer along with water molecules [4–6]. As-prepared HTCs typically contain carbonates as compensating anions which makes these materials inactive in base-catalyzed reactions [7]. Thermal treatment of Mg–Al HTCs results in decomposition of carbonate groups accompanied by the release of  $\text{CO}_2$  and the formation of a well-dispersed mixture of magnesium and aluminum oxides (MgAlO). The calcined mixed oxides act as weak Lewis acid/strong base catalysts and find various applications

as effective catalysts in transesterification [8,9], alcohol elimination [10] and condensation [11,12] reactions. A distinctive feature of MgAlO materials is their ability to reconstruct the lamellar HTC structure (so-called memory effect) when contacted with water vapor or liquid water in absence of carbon dioxide. This leads to meixnerite (magnesium aluminium hydroxide hydrate), that is HTC intercalated with  $\text{OH}^-$  as compensating anions in the interlayer [11,12]. In addition, the treatment of MgAlO with aqueous reaction mixture (*in situ* rehydration) leading to reconstructed HTCs is also known [12–14]. These rehydrated materials have been applied to a number of base-catalyzed reactions which require Brønsted basic character, including different self- and cross-condensations [12–15] Michael additions [16], etc.

Condensation reactions attract much attention because they allow obtaining more complex compounds with more carbon atoms starting from relatively simple molecules. The interest in these reactions stems from the fact that many of the initial molecules for the syntheses can be obtained by biomass processing. For example, furfural can be obtained by acid hydrolysis of sugar cane bagasse, a residue from sugar cane processing, followed by extraction [17]. The needed acetone may be obtained by ketonization of acetic acid [18] that is an important product

\* Corresponding author.

E-mail address: [oleg.kikhtyanin@unicr.cz](mailto:oleg.kikhtyanin@unicr.cz) (O. Kikhtyanin).

of biomass pyrolysis. Aldol condensation of these relatively simple molecules allows increasing chain length to 8+ carbon atoms. This route has attracted significant interest, because hydrogenation/hydrodeoxygenation of these aldol condensation products leads to various hydrocarbons suitable for blending in conventional diesel fuel and kerosene [19]. A comprehensive study of aldol condensation over solid catalysts is thus necessary for designing the pathway to components of motor fuels from renewable natural resources.

Aldol condensation of furfural (F) and acetone (Ac) in the presence of a basic catalyst begins with the initial abstraction of the  $\alpha$ -proton from acetone, forming a carbanion that consecutively attacks the carbonyl group of the nearby adsorbed furfural molecule [20,21]. Additionally, acetone can be transformed on basic (or acidic as well) sites by its own reaction pathway which is acetone self-condensation resulting to the formation of diacetone alcohol, mesityl oxide, etc [11,13]. Both aldol condensation of furfural with acetone and acetone self-condensation can proceed simultaneously; in this case the rate-determining step should be shared by both reaction pathways and involve basic sites with similar strength [20].

Much less attention is paid to the transformation of furfural on basic sites of a solid catalyst in absence of acetone, or generally in absence of carbonyl compounds having no  $\alpha$ -hydrogen atoms. Nevertheless, furfural can hardly be considered as an inert component when contacted with basic sites and a specific parallel reaction route has to be considered. Cannizzaro reaction (CR) is a well-known base-induced redox reaction of an aldehyde lacking a hydrogen atom in the alpha position. It represents the disproportionation of an aldehyde into a carboxylic acid and an alcohol catalyzed by a strong aqueous base, i.e. it takes two aldehydes to produce one acid and one alcohol. In case of furfural, two furfural molecules would produce furfuryl alcohol (F-OH) and furoic acid (F-OOH) according to the reaction scheme below (Scheme 1).

The mechanism of the CR is well postulated. The reaction begins with the attack of hydroxide from basic NaOH on the carbonyl carbon followed by deprotonation to give a dianion. This unstable intermediate releases a hydride anion which attacks another molecule of aldehyde. In this process the dianion converts to a carboxylate anion and the aldehyde to an alkoxide. The alkoxide then picks up a proton from water to provide the alcohol final product, while the carboxylate is converted to the carboxylic acid product after acid work-up [22]. It should be mentioned that in aqueous basic solution carboxylic acid produced by CR can hardly be detected in pure form as it immediately reacts with the base to form a corresponding salt.

Taking into account the scheme of furfural transformation by CR the occurrence of this reaction on a basic solid can also be assumed provided that the catalyst possesses hydroxides of sufficient strength as active sites and the reaction proceeds in aqueous medium. Indeed, this reaction was proposed among others when considering all possible reactions occurring during aqueous furfural aldol condensation with acetone using base solid catalysts [23]. Additionally, it was mentioned that MgO in aqueous media could catalyze the formation of the intermediate species for the Cannizzaro reaction (furfuryl alcohol and furoic acid) resulting in the formation of esterification product, 2-furancarboxylic 2-furanmethyl ester (furoyl furoate, FF) [24]. Nevertheless, there is no information available on the effect of CR on the physico-chemical properties of a solid basic catalyst as well as on its impact on the behavior of the catalyst in aldol condensation.

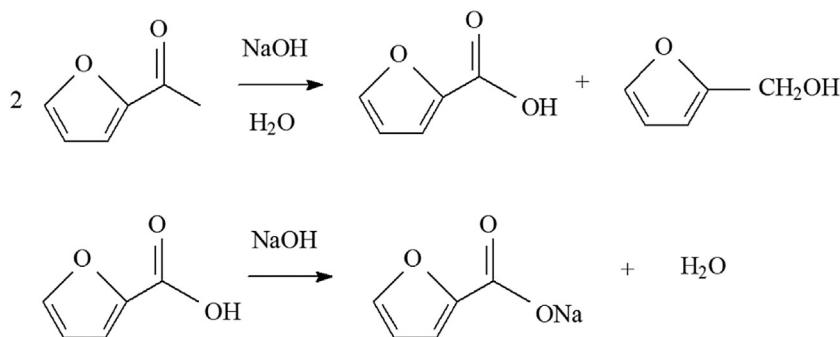
The scope of the present work is thus to understand the behavior of calcined Mg–Al mixed oxide as a catalyst for converting aqueous furfural mixture and to provide information on the extent of CR and its impact on the catalyst performance in aldol condensation.

## 2. Experimental

Mg–Al layered double hydroxalcalite (HTC) with a Mg:Al molar ratio of 3:1 was prepared according to a procedure described in [25]. The Mg–Al mixed oxide was prepared by calcination of the dried as-prepared HTC at 450 °C for 3 h (heating rate 5 °C/min). The rehydration of the mixed oxide was performed by its stirring in water (2 g of freshly calcined material per 30 mL of water) at room temperature for 30 min, followed by the filtration of resulting solid with a vacuum pump and drying in a rotary evaporator in N<sub>2</sub> flow during 40 min. The calcined HTC is further on referred to as Mg–Al mixed oxide while the fully rehydrated mixed oxide is denoted as reconstructed HTC.

The crystallographic structures of the dried as-prepared HTC sample, Mg–Al mixed oxide and materials obtained during rehydration experiments were determined by X-ray powder diffraction using a Philips MPD 1880 instrument with Cu K $\alpha$  irradiation ( $\lambda = 0.154$  nm) in the  $2\theta$  range of 5°–70° with the  $2\theta$  scanning rate of 2.4°/min. The relative content of present crystalline phases in the solids was evaluated using the areas of diffraction peaks at  $2\theta = 11.4$  and 22.8° for the HTC phase and at  $2\theta = 43.1$ ° for the MgO phase, wherein the relative content of the respective phases in as-synthesized HTC and Mg–Al mixed oxide were taken as 100%. The textural properties of the samples (specific surface area and pore volume) were measured by nitrogen physisorption at –196 °C using an Autosorb surface area and porosity analyzer. The basic properties of as-prepared HTC were evaluated by temperature programmed desorption (TPD) of carbon dioxide in a Micromeritics Autochem 2950 apparatus. Before reduction, the sample was outgassed under a He flow of 25 cm<sup>3</sup> min<sup>–1</sup> with a heating ramp of 10 °C min<sup>–1</sup> up to 500 °C. The sample was cooled down to 50 °C and saturated under a CO<sub>2</sub> flow (10 vol.% in He) of 50 cm<sup>3</sup> min<sup>–1</sup> for 30 min. Subsequently, the physically adsorbed carbon dioxide was removed by flowing He (25 cm<sup>3</sup> min<sup>–1</sup>) at 50 °C for 60 min. Finally, the chemically absorbed CO<sub>2</sub> was desorbed by heating up the sample to 850 °C (heating rate of 15 °C min<sup>–1</sup>) in flowing He (25 cm<sup>3</sup> min<sup>–1</sup>) and maintaining this temperature for 30 min. The amounts of desorbed species were quantified using calibration standards. Thermogravimetric analysis of the dried as-prepared HTC catalysts was performed using a TA Instruments TGA Discovery series equipment operating with a heating ramp of 10 °C/min from room temperature to 900 °C in N<sub>2</sub> flow. TGA-MS experiments were performed on the same TGA unit equipped with mass-spectrometer OmniStar GSD 320 (Pfeiffer-Vacuum) with MID (Multiple Ion Detection) measurement mode, SEM (Secondary Electron Multiplier) detector and quadrupole mass analyzer. The DRIFT spectra were recorded on a Nicolet IS 10 FTIR spectrometer equipped with DTGS detector and KBr beam splitter. All spectra were collected over the range of 4000–400 cm<sup>–1</sup> at a spectral resolution of 4 cm<sup>–1</sup> and number of scans 128 (both for the background and the sample spectra).

Furfural (Sigma-Aldrich) used for the study was pre-dried with a molecular sieve 3A to exclude the influence of moisture originating from the chemicals. All catalytic experiments on furfural conversion using either water-free conditions or aqueous furfural mixture were carried out in a 100 mL stirred batch reactor (a glass flask reactor) operating at T = 50 °C. Furfural conversion as a function of reaction time was studied in experiments using 2 g of freshly calcined HTC (or rehydrated HTC prepared from the same amount of Mg–Al mixed oxide) and 30 g of furfural. To prepare aqueous furfural mixtures, different amount of water (ranging from 0 to 33wt.%) was added to furfural. As the solubility of water and F in each other is limited [26], aqueous furfural mixtures with water content  $\leq 6$  wt.% were monophasic solutions while higher water amounts resulted in the formation of a biphasic (water and organic phases) mixtures if no stirring was used. To ensure



**Scheme 1.** Cannizzaro reaction in the presence of sodium hydroxide as a basic catalyst.

a “quasi-constant” reaction conditions, the reaction mixture was stirred at 300 RPM to afford aqueous organic emulsion. After adding the catalyst to the reaction mixture, the reaction was carried out at  $T=50^{\circ}\text{C}$  for 180 min at 300 RPM. Samples were periodically withdrawn from the reactor during the experiment, filtered, and analyzed by Agilent 7890A GC unit equipped with a flame ionization detector (FID), using a HP-5 capillary column (30 m/0.32 mm ID/0.25  $\mu\text{m}$ ). The obtained products were identified based on standard reference compounds as well as additional GC–MS analyses. The catalytic results of furfural transformation over basic catalysts were described in terms of product yield that was calculated as follows:

$$\text{Yield of product } i(t)(\text{mol}\%) = 100 \times (\text{mole of reactant converted to product } i)_{t/\text{reactant } t=0}$$

After the reaction the catalysts were separated from aqueous furfural mixture by filtration, washed with ethanol, dried in  $\text{N}_2$  flow at room temperature and characterized by different methods. Catalysts obtained from experiments with aqueous furfural mixtures having different water content are denoted HTC-xx where xx stands for the wt.% of water in the mixture, i.e. HTC-23 is a catalyst obtained from reaction in which aqueous furfural containing 23 wt.% of water was used as feedstock.

Aldol condensation of furfural and acetone was performed by using the same stirred batch reactor operating at  $T=50^{\circ}\text{C}$ . For these experiments 0.5 g of freshly calcined HTC, 6.5 g of furfural and 19.7 g of acetone (Ac:F = 5 mol/mol) were used. After adding the catalyst to the reaction mixture, the reaction was carried out at  $T=50^{\circ}\text{C}$  for 180 min under intensive stirring. Samples were periodically withdrawn from the reactor during the experiment, filtered and analyzed by the same GC method. Catalytic results of aldol condensation of furfural and acetone were described by conversion parameter that was calculated from the corresponding molar concentrations as follows:

$$\text{Reactant conversion } (t)(\text{mol}\%) = 100 \times (\text{reactant}_{t=0} - \text{reactant}_t) / \text{reactant}_{t=0}$$

### 3. Results

#### 3.1. Catalyst characterization

The physico-chemical properties of as-prepared HTC, calcined HTC (Mg–Al mixed oxide) and rehydrated HTCs investigated by XRD, TGA/DTG and DRIFT are presented in Table 1 and the Supplementary information (SI).

The XRD pattern of the freshly synthesized sample used in this study (see SI) shows a pure hydrotalcite phase (JCPDS 22-700) with intensive symmetrical peaks at  $2\theta \approx 11^{\circ}$ ,  $22.8^{\circ}$ ,  $36^{\circ}$  and  $60^{\circ}$ , which are characteristic for the brucite-like layers. No additional crystalline phases could be identified in the diffractogram proving the high phase purity of the as-prepared hydrotalcite material. The XRD pattern of the sample calcined at  $450^{\circ}\text{C}$  (Mg–Al mixed oxide) confirms the disappearance of the layered HTC structure. The only reflections observed in the XRD pattern (see SI) correspond to the MgO phase proving the formation of Mg–Al mixed oxide with the MgO periclase-type structure (JCPDS 87-0653). XRD pattern of a sample obtained after interaction of the Mg–Al mixed oxide with liquid water evidences the presence of a reconstructed HTC phase (meixnerite, JCPDS 35-0965) (see SI). It is worth noting that the XRD patterns of totally rehydrated samples shows neither a significant loss in intensity nor broadening of XRD peaks in comparison with the as-prepared HTC., i.e. these samples can be considered to be reconstructed HTCs. It also means that upon mechanical stirring during the rehydration process in liquid phase the hydrotalcite-like platelets were not broken or exfoliated which would result in a decrease in their particle size and in a change in their textural properties.

The textural properties of the as-prepared and Mg–Al mixed oxide (Table 1) are similar to those obtained for similar materials in our other studies [25]. According to chemical analysis, Mg/Al molar ratio in as-prepared material is 3.8 (Table 1), i.e. slightly higher when compared with the starting concentration of the elements in reactive synthesis gel. Assuming that each Al atom in the solid should produce one basic site, the theoretically possible concentration of basic sites in the sample with Mg/Al = 3.8 (with respect to bulk Al content) is 4.9 mmol/g for calcined sample, i.e. Mg–Al mixed oxide, (Table 1) or 2.7 mmol/g for dried as-prepared HTC taking into account its general formula and weight loss upon calcination (TGA data see below).

The actual concentration of basic sites was measured by  $\text{CO}_2$ -TPD technique. The uptake of  $\text{CO}_2$  was 0.85 mmol per one gram of dried as-prepared HTC sample used in the experiment, hence the total concentration of basic sites determined by  $\text{CO}_2$ -TPD was 0.85 mmol/g based on the as-prepared HTC or 1.54 mmol/g if recalculated for Mg–Al mixed oxide, i.e. nearly 31.5% of theoretical value (Table 1).

The TGA profile for the as-prepared HTC sample (see SI) is in good agreement with the profiles reported in literature for HTC-like materials [27,28]. The total weight loss for this sample amounts to 45.8 wt.% (Table 2) which is in accordance with previous results [27,28]. The low temperature weight loss of 16.7 wt.% occurs in the range of  $20$ – $200^{\circ}\text{C}$  due to the removal of water molecules. It is clearly seen (see SI) that the signal in this range could be deconvoluted in two peaks with maxima at ca.  $100$  and  $200^{\circ}\text{C}$  which are generally attributed to the loss of physically adsorbed and interlayer water molecules, correspondingly [27]. The high tem-

**Table 1**  
Physico-chemical characteristics of Mg-Al samples used in the present study.

| Sample                   | Phase composition | BET area (m <sup>2</sup> /g) | Mg/Al in synthesis gel (mol/mol) | Mg/Al by XRF (mol/mol) | Theoretical amount of basic sites (mmol/g) | Concentration of basic sites by CO <sub>2</sub> -TPD (mmol/g) |
|--------------------------|-------------------|------------------------------|----------------------------------|------------------------|--|---|
| HTC <sub>as-prep.</sub>  | HTC               | –                            | 3                                | 3.8                    | 2.7  | 0.85  |
| Mg-Al <sub>calc.</sub>   | MgO               | 180                          |                                  |                        | 4.9  | 1.54  |
| HTC <sub>reconstr.</sub> | HTC               | –                            |                                  |                        | 2.7  |   |

**Table 2**  
Results on the thermal analysis of the samples and their formula calculated from TGA-MS data.

| Sample                   | Weight loss (TGA), % |           |            | Calculated formula (using TGA-MS)   |
|--------------------------|----------------------|-----------|------------|---|
|                          | Total                | 20–250 °C | 250–800 °C |   |
| HTC <sub>as-prep.</sub>  | 45.8                 | 16.7      | 29.1       | Mg <sub>7.6</sub> Al <sub>2</sub> CO <sub>3(1.08)</sub> OH <sub>19.6</sub> ·6.2H <sub>2</sub> O |
| Mg-Al <sub>calc.</sub>   | 10.2                 | 4         | 6.2        | –   |
| HTC <sub>reconstr.</sub> | 45.4                 | 17.1      | 28.3       | Mg <sub>7.6</sub> Al <sub>2</sub> CO <sub>3(0.16)</sub> OH <sub>21</sub> ·8.2H <sub>2</sub> O   |

perature weight loss of 29.1 wt.% is observed at temperature above 200 °C and originated from the dehydroxylation of the brucite-like sheets and the decomposition of carbonates in the interlayer [27]. To quantify the ratio between hydroxyl and carbonate groups in the as-prepared HTC, TGA-MS technique was used to determine H<sub>2</sub>O and CO<sub>2</sub> evolution from the sample. Above 250 °C, the MS spectra show the presence of signals of H<sub>2</sub>O and CO<sub>2</sub> (see SI) with the maxima at similar temperature, i.e. 395 and 404 °C, correspondingly, which prevents their differentiation by a routine TGA analysis. Using data from chemical and thermal analysis, the composition of the as-prepared hydrotalcite was calculated being very close to expectations from theory (Table 2).

In comparison with the as-prepared HTC, the weight loss of the calcined material (i.e. Mg-Al mixed oxide) is, as expected, much lower (only 10.2 wt.%) (Table 1). It corresponds to the loss of the physically adsorbed water below 100 °C (4.0 wt.%) and the removal of residual hydroxyls and carbonate groups at T ≥ 500 °C remained present after the sample calcination at T = 450 °C (see SI). Total weight loss in the rehydrated sample is 45.4 wt.% (Table 1), i.e. very close to the value determined for the as-prepared HTC material. The distribution and intensity of the signals observed in the DTG spectra for the as-prepared and the reconstructed samples are also similar. Nevertheless, the performed TGA-MS study of both samples evidences a substantial decrease in the intensity of the signal corresponding to the evolved CO<sub>2</sub> (see SI). It proves that as a result of the calcination-rehydration procedure most of the carbonate groups are replaced by hydroxyls in the reconstructed HTC as evidenced by the calculated formula of the reconstructed HTC (Table 2). The observed presence of carbonate groups in the reconstructed HTC results most probably from the interaction of the rehydrated sample with CO<sub>2</sub> from air before the TGA analysis.

The DRIFT spectrum of the as-synthesized HTC material (see SI) is similar to the spectra published elsewhere [1,12,29,30]. A typical broad band at about 3460–3500 cm<sup>-1</sup> is attributed to the stretching vibrations of structural hydroxyl groups in the brucite-like layer. A shoulder at 3000 cm<sup>-1</sup> is assigned to hydrogen bonding between water molecules and the interlayer carbonate anions. The bands at around 1640 and 1370 cm<sup>-1</sup> confirms the expected presence of interlayer water molecules and carbonate (chelating or bridging bidentate) anions, respectively. The vibration at 1515 cm<sup>-1</sup> is ascribed to a reduction in the symmetry caused by the presence of monodentate carbonates ( $\gamma_{\text{asymO-C-O}}$ ) interacting with Mg<sup>2+</sup>, as reported elsewhere [1,12,29,30]. The low frequency region shows a band at about 560 cm<sup>-1</sup>, corresponding to the translation modes of hydroxyl groups, influenced by Al<sup>3+</sup> cations [12,31,32]. The band at 870 cm<sup>-1</sup> is characteristic for the out-of-plane deformation of carbonate, whereas the in-plane bending is located at 680 cm<sup>-1</sup> [12].

Calcination of the as-prepared HTC results in water removal that is evidenced by the disappearance of the band at around 1640 cm<sup>-1</sup> (water bending vibrations) and of the shoulder at 3000 cm<sup>-1</sup> (interaction of H<sub>2</sub>O–CO<sub>3</sub><sup>2-</sup> in the interlayer) (see SI). The intensity of the bands at around 3460–3500 cm<sup>-1</sup> also decreases due to the surface dehydroxylation upon calcination. The band at 1370 cm<sup>-1</sup> (interlayer carbonates) decreases in intensity and the two peaks at about 1515 and about 1400 cm<sup>-1</sup> evidencing the interaction between CO<sub>3</sub><sup>2-</sup> and Mg<sup>2+</sup> [12] are also present, but their intensity decreases as well. The obtained FTIR spectrum proves that residual carbonate and hydroxyls anions as well as small amount of water (band at around 1640 cm<sup>-1</sup>) are still present in HTC sample calcined at T = 450 °C, i.e. in the Mg-Al mixed oxide sample, most likely due the adsorption of CO<sub>2</sub> and moisture from air during the DRIFT experiment.

The spectrum of the reconstructed HTC is substantially similar to that of the as-prepared HTC (see SI). The broad band at 3460–3500 cm<sup>-1</sup> evidences the recovery of the structural hydroxyl groups in the brucite-like layers. The bands at 3050 and 1640 cm<sup>-1</sup> also reappears in the spectra of this sample, indicating a significant amount of adsorbed water molecules in the reconstructed material. The band at 1370 cm<sup>-1</sup> which also reappears in the spectra as a symmetric peak is usually attributed to the presence of carbonates in reconstructed materials, even after rehydration step [12,32]. In the latter case, the existence of these groups in the rehydrated samples is explained by a probable introduction of (CO<sub>3</sub>)<sup>2-</sup> from air during the reconstruction process [12]. However, the performed TGA-MS analysis of the reconstructed HTC proves low concentration of carbonates in the reconstructed HTC, so the band at 1370 cm<sup>-1</sup> in DRIFT spectrum cannot be unequivocally attributed to carbonate groups. Moreover, anionic OH-groups should be inevitably identified in the DRIFT spectra of the reconstructed HTC material as well. It is known that anionic groups other than carbonates could be characterized by absorption bands in the FTIR region close to 1370 cm<sup>-1</sup>. For example, a band at 1364 cm<sup>-1</sup> was previously ascribed to the anti-symmetrical stretching mode of nitrate ions [33] and a band observed at 1390 cm<sup>-1</sup> was attributed to the symmetric stretching of the carboxylate group [34]. Hence, hydroxyl groups formed due to the rehydration of Mg-Al mixed oxide (calcined HTC), which compensate the positive charge of the layers, could be also responsible for the observed band lying in the same FTIR-region. This makes us to conclude that the band at 1370 cm<sup>-1</sup> could in fact signify the presence of any extra-framework functional anionic groups, including OH<sup>-</sup>, which compensate the positive charge of the inorganic framework originating from the Mg-Al isomorphous substitution.

### 3.2. Interaction of Mg-Al mixed oxide with aqueous furfural mixture

According to the reaction scheme (Scheme 1), water is a necessary participant of Cannizzaro reaction donating a proton for an intermediate alkoxide to be converted to a final alcohol. In other words, the absence of water makes the disproportionation of furfural to furfuryl alcohol (F-OH) and furoic acid (F-OOH) in the presence of a basic catalyst impossible. Accordingly, in our experiments we have studied the behavior of Mg-Al mixed oxide in CR of aqueous furfural solutions having different water content.

The main reaction products obtained by reaction of aqueous furfural feedstock over calcined HTC, i.e. over Mg-Al mixed oxide, are F-OH and furoyl furoate (FF). Despite no F-OOH is found in reaction products, the formation of F-OH and FF, a product of esterification reaction between F-OH and F-OOH, provides an indirect evidence that furfural undergoes CR over the solid base catalyst. One-stage alcohol formation from aldehyde is only possible by using hydrogen atmosphere and a hydrogenation catalyst which is not the case in our experiment. Moreover, due to the basic nature of the catalyst used it is highly likely that F-OOH will react immediately with the basic sites forming either salts, e.g. sodium furoate when NaOH would be used as catalyst, or surface furoates in case of solid base catalysts. This is confirmed by a titration experiment (see SI) in which F-OOH is successively added to Mg-Al mixed oxide (calcined HTC) catalyst immersed in acetone followed by GC analysis of the liquid phase. A signal on the GC diagram belonging to F-OOH appears only when the amount of acid added to the catalyst exceed 0.3 g/g<sub>cat</sub>. The only plausible explanation of the performed titration experiment is that the acid remains adsorbed on the catalyst. It is worth noting that the concentration of basic sites in the calcined sample titrated with F-OOH is  $\approx 2.7$  mmol/g, which is higher than that determined by CO<sub>2</sub>-TPD (based on Mg-Al mixed oxide). Presumably, furoic acid could additionally adsorb on weak basic sites which do not interact with CO<sub>2</sub> in the CO<sub>2</sub>-TPD experiment. Assuming the formation of surface furoates, we have introduced the yield of F-OH as the measure of catalyst activity in Cannizzaro reaction.

Fig. 1A depicts F-OH yield observed during reaction of aqueous furfural mixtures having different water content on Mg-Al mixed oxide in dependence on experiment duration. A clear dependence of catalyst activity on water content in the mixture is observed. At water-free conditions, F-OH yield is as low as 0.11 wt.% after 180 min of the reaction. This result confirms the necessity of water presence in the reaction mixture to facilitate the Cannizzaro reaction, which is in accordance with the reaction scheme (Scheme 1). The catalyst activity observed in the water-free experiment can be explained by the traces of moisture in the sample due to adsorption from air during the transfer of the calcined catalyst into the reactor. This explanation is also supported by TGA results. The observed alcohol yield corresponds to 0.15 mmol of F-OH produced per 1 g of Mg-Al mixed oxide. Taking into account the reaction stoichiometry, i.e. the equimolar formation of F-OH and F-OOH, and assuming acid-base interaction between the formed F-OOH and basic sites of the catalyst, it can be inferred that about 10% of the basic sites in the catalyst probed by CO<sub>2</sub> (Table 1) participate in the reaction and react with the produced acid forming furoate species.

Fig. 1A shows that the increase in water content in the mixture results in the growth of F-OH yield proving thus the importance of water in the reaction (Scheme 1). For monophasic reaction conditions (water content in the range of 0–6 wt.%) the F-OH yield is below 0.5 wt.% after 180 min of the reaction. Under biphasic reaction conditions (water content >12 wt.%) the F-OH yield substantially increases to 1.8–2.3 wt.% (Fig. 1A). The maximum alcohol yield of 2.3 wt.% is observed for water content of 23 wt.% in the mixture while further increase in water content up to 33% results in a slight decrease of F-OH yield to 1.9 wt.%.

The maximum F-OH yield of 2.3 wt.% (Fig. 1A) corresponds to 3.6 mmol of produced F-OH per 1 g of calcined catalyst. Hence, the amount of the produced acid should also correspond to 3.6 mmol<sub>F-OOH</sub>/g<sub>cat</sub>. Since F-OOH is not identified by GC among reaction products, the concentration of basic sites that interacted with the acid should also be equal to 3.6 mmol/g<sub>cat</sub>. This value is larger than that determined by the direct titration of Mg-Al mixed oxide with furoic acid (see SI) and substantially exceeds the value determined by CO<sub>2</sub>-TPD (Table 1). On the other hand, the concentration of basic sites in the catalyst evaluated from its activity in CR is still lower than the theoretical basicity derived from its chemical composition. It allows concluding that not all basic sites in the catalyst are involved in the reaction and the formation of surface furoates. Nevertheless, the concentration of basic sites as high as 3.6 mmol/g determined by the *in-situ* “titration” with furoic acid proves that physico-chemical characteristics of basic catalysts including the amount of basic sites can change during the rehydration step as discussed below.

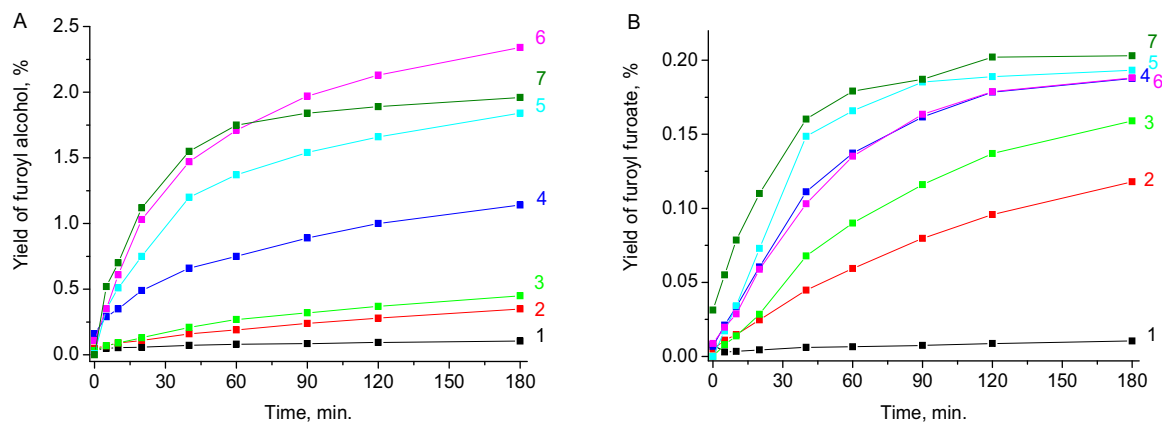
Besides F-OH, furoyl furoate is observed as a reaction product (Fig. 1B), apparently as a result of esterification reaction between furfuryl alcohol and furoic acid. In contrast to F-OH, the yield of the FF ester exhibits a less pronounced dependence on water content. Fig. 1B shows that after 180 min of the reaction, the ester yield is 0.16 wt.% for monophasic aqueous furfural mixture ( $\leq 6$  wt.% of water) and only small increase to 0.18–0.2 wt.% is observed for higher water contents (biphasic reaction mixture). The observed poor dependence of the ester yield on water content allows assuming that the formation of this compound could be more preferable in water-free reaction conditions. Obviously, as water is a product of the esterification reaction, an increase in water content will favor hydrolysis over esterification, i.e. shift the reaction equilibrium towards the reactants.

### 3.3. The properties of Mg-Al catalysts after reaction

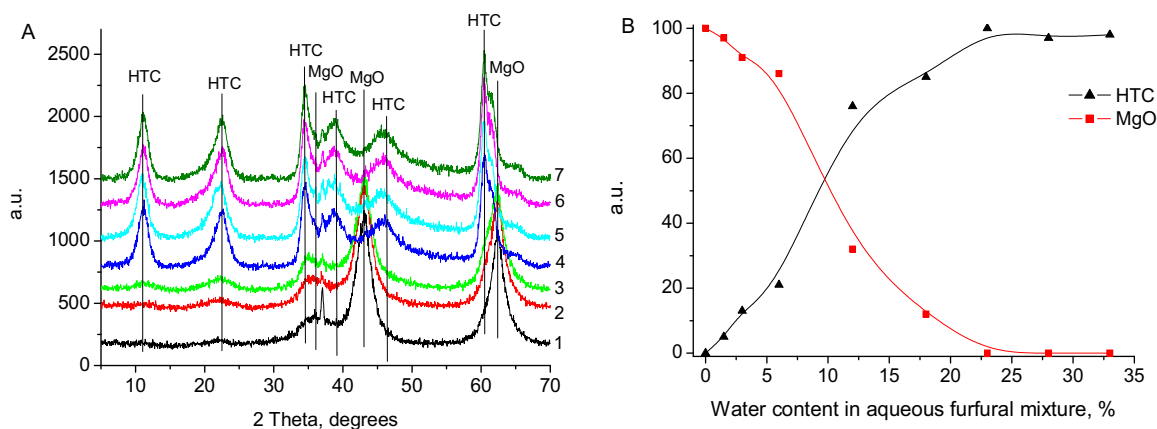
The experimental results provide a strong indication that furfural is converted by Cannizzaro reaction over Mg-Al mixed oxide when water is present. Whereas F-OH is observed in the reaction products by GC, it is highly probable that F-OOH forms furoate species on the catalyst surface, i.e. remains adsorbed on the basic sites of the catalyst. The formation of such species would definitely change physico-chemical properties of a basic catalyst and these have been monitored by different techniques.

#### 3.3.1. XRD

Fig. 2A depicts XRD patterns of catalysts after reaction in dependence on water content in aqueous furfural mixture. XRD patterns of samples after experiments using a monophasic reaction mixture (water content of 0–6 wt.%) contain predominantly reflections characteristic for MgO phase. As soon as the furfural mixture becomes biphasic (water content  $\geq 12$  wt.%), the intensity of the reflections due to the MgO phase noticeably decreases while the intensity of reflections corresponding to the HTC phase increases. The calculated relative content of the crystalline phases (Fig. 2B) evidences that a dramatic step change in the phase composition of the catalysts occurs when the monophasic reaction mixture turns into a biphasic one due to the increase in water concentration. In the monophasic aqueous-organic mixture the probability for the inorganic solid to interact with water molecules (a necessary step for rehydration to take place) is low because of high furfural concentration because both molecules compete for the same adsorption places. As a consequence, the rehydration of the mixed oxide to a reconstructed HTC is slow. In contrast, when the reaction mixture is biphasic, the catalyst is in contact with both organic (mostly furfural) and aqueous (mostly water) phases. The XRD data evidence (Fig. 2) that such intermittent interaction of Mg-Al mixed



**Fig. 1.** Yields of furfuryl alcohol (A) and furfuryl furate (B) observed during reaction of aqueous furfural mixture on Mg-Al mixed oxide in dependence on water content (in wt.%): 1–0%, 2–3%, 3–6%, 4–12%, 5–18%, 6–23%, 7–33%.  $T_{\text{reac.}} = 50^\circ\text{C}$ ,  $m_{\text{furfural}} = 30\text{ g}$ ,  $m_{\text{calc.cat.}} = 2\text{ g}$ .



**Fig. 2.** XRD patterns (A) and the relative content of HTC and MgO phases (B) in catalysts after reaction in dependence on concentration of water in aqueous furfural mixture: 1–HTC-0, 2–HTC-3, 3–HTC-6, 4–HTC-12, 5–HTC-18, 6–HTC-23, 7–HTC-33 where the numbers denote wt.% of water in the mixture.

oxide with either organic or aqueous phase under intensive stirring ensures the transformation of the solid mixed oxide into reconstructed HTC. The comparison of the catalytic results with the XRD data allows concluding that the observed high activity of the catalysts in CR is connected with the high rehydration degree of Mg-Al mixed oxide to a reconstructed HTC. This conclusion is in agreement with the reaction scheme of CR: the disproportionation of furfural to F-OH and F-OOH takes place with the participation of hydroxyls which are Brønsted basic sites of the rehydrated HTC catalyst rather than with the Lewis basic sites of Mg-Al mixed oxide.

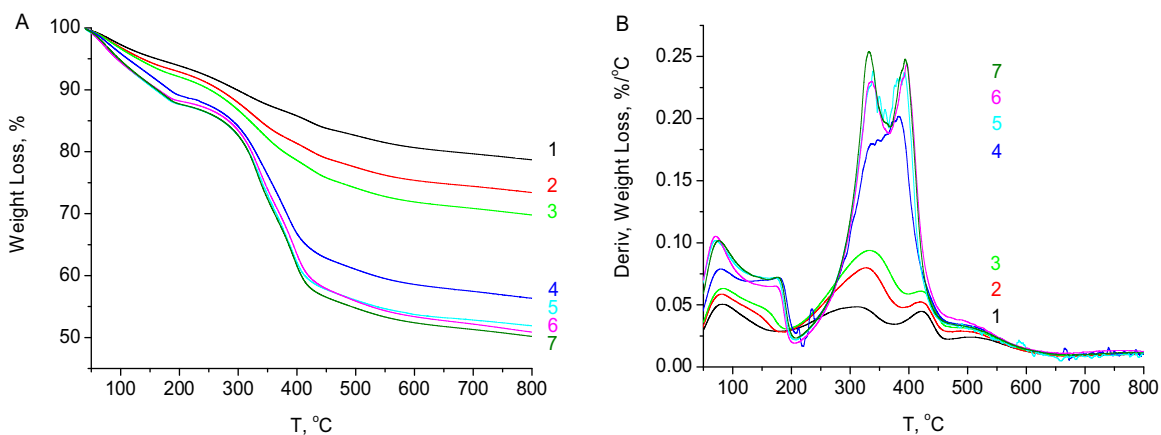
### 3.3.2. TGA

Fig. 3A depicts TGA curves of the catalyst samples after Cannizzaro reaction of furfural aqueous mixtures having variable water content. The catalysts were separated from reaction mixtures by filtration followed by washing with ethanol and drying at  $80^\circ\text{C}$  for 4 h before TGA experiments to exclude the contribution of any physisorbed organic species to the results. The increase in water content results in a progressive increase in the total weight loss of the samples (Fig. 3A) which correlates with the transformation of the Mg-Al mixed oxide to reconstructed HTC materials as proved by XRD (Fig. 2). The samples obtained from the reaction of monophasic furfural-water mixtures possess low-to-moderate weight loss in the range of 21–30 wt.%, due to the small rehydration degree of the Mg-Al mixed oxide (<20%). In contrast, the weight loss of the sample HTC-23 obtained after reaction of biphasic furfural-water mixture amounts to 49 wt.% which is close to the values for as-prepared or water-reconstructed HTC samples (Table 1). In

agreement with these results, the sample HTC-23 affords a nearly fully reconstructed HTC after the reaction as evidenced by the XRD results (Fig. 2).

The DTG curves of the samples after reaction (Fig. 3B) show two ranges of weight losses in accordance with the results for as-prepared or reconstructed HTC samples. The low-temperature region consists of two signals at  $T = 80\text{--}100^\circ\text{C}$  and  $180\text{--}200^\circ\text{C}$  attributed to physically adsorbed and interlayer water, respectively, the latter exhibiting a clear dependence on the reconstruction degree of the rehydrated samples. In fact, the change in phase composition is linearly proportional to the water content in the aqueous furfural mixture. In agreement with the XRD data (Fig. 2A) an obvious difference is observed between the TGA/DTG curves for samples obtained from monophasic or biphasic reaction mixture experiments.

In the high-temperature region of DTG curves, the presence of two well-distinguished signals at  $\sim 320$  and  $\sim 400^\circ\text{C}$  can be observed. The signal at  $T = 385\text{--}400^\circ\text{C}$  is similar to those observed in both as-prepared and reconstructed HTC samples and corresponds to the removal of carbonate and/or hydroxyl groups from the samples [27]. For the catalysts after reaction the intensity of this peak increases with the growth in water content in the reaction mixture and, as a consequence, it is in line with the increase in the rehydration degree of Mg-Al mixed oxide proved by XRD (Fig. 2). Nevertheless, the signal with maximum at  $T = 320^\circ\text{C}$  was not previously observed in DTG curves for as-prepared and water-reconstructed HTC materials (see SI). Therefore, this signal has to originate from other compounds than water,  $\text{CO}_2$  or contaminants



**Fig. 3.** TGA (A) and DTG (B) curves of catalysts obtained after reaction with aqueous furfural mixture with different water content. 1–HTC-0, 2–HTC-3, 3–HTC-6, 4–HTC-12, 5–HTC-18, 6–HTC-23, 7–HTC-33.

from ambient air, i.e. from furfural or reaction products of furfural transformation including F-OH, F-OOH and FF. The intensity of this signal also increases with the increasing concentration of water in the reaction mixture. As the increase in the water content resulted in an increase in the furfuryl alcohol yield (Fig. 1A), it can be deduced that the signal at  $T=320^{\circ}\text{C}$  is due to furfuryl alcohol or, more likely, due to surface furoates formed by adsorption of furoic acid that is produced from furfural by Cannizzaro reaction in equimolar yields as furfuryl alcohol, but unlike F-OH is not detected among reaction products.

### 3.3.3. DRIFT

DRIFT spectra obtained after contacting Mg-Al mixed oxide with aqueous furfural mixtures having different water content are shown in Fig. 4 (reconstructed HTC rehydrated with pure water is shown as a reference). With increasing water content, a broad band in the range of  $2700\text{--}3700\text{ cm}^{-1}$  reappears in the spectra proving the recovery of structural hydroxyl groups in the brucite-like layers of the rehydrated samples (Fig. 4A). The bands in the range of  $1300\text{--}1700\text{ cm}^{-1}$  which characterize the presence of interlayer water molecules and compensating extra-framework anions also appear in the spectra (Fig. 4B). The change of the DRIFT spectra for Mg-Al mixed oxide sample after its contact with aqueous medium can be attributed to the HTC structure recovery and is thus in agreement with XRD and TGA results. However, comparing the DRIFT spectra for catalysts after reaction with the spectra for both as-prepared and rehydrated HTC samples, it can be concluded that the composition of the functional groups in the samples after reaction is different than in the fresh samples. First, shoulder at  $3000\text{ cm}^{-1}$  usually observed in the DRIFT spectra of both as-prepared and reconstructed HTC rehydrated with pure water is absent in the DRIFT spectra of the spent catalysts. The absence of this shoulder suggests that the  $\text{H}_2\text{O}\text{--CO}_3^{2-}$  interaction in the interlayer is weakened. Furthermore, the character of the bands in the range of  $1300\text{--}1700\text{ cm}^{-1}$  differs: it becomes more complex for the samples after reaction as additional bands appeared in the spectra (Fig. 4B). Instead of a single band at  $1640\text{ cm}^{-1}$  which characterizes the presence of water molecules in interlayer (Fig. 2) several bands at  $1561$  and  $1591$  are present in the DRIFT spectra of catalysts after reaction. These bands suggest that other molecules than water are present in the interlayer of the rehydrated catalysts. Moreover, two new bands at  $1363$  and  $1390\text{ cm}^{-1}$  are also present in the spectra. For as-prepared and reconstructed HTC rehydrated with pure water the band at  $1370\text{ cm}^{-1}$  characterizes the presence of compensating anions, as discussed above. The appearance of the new bands at  $1363$  and  $1390\text{ cm}^{-1}$  can be related with the presence of new kind

of compensating anions, such as furoates. Besides, a well-expressed band at  $1479\text{ cm}^{-1}$  not observed previously in the DRIFT spectra for neither as-prepared nor rehydrated HTC samples is found in the spectra of spent catalysts. Finally, several new bands appeared also in the range of  $900\text{--}1250\text{ cm}^{-1}$  (Fig. 4B) which could be caused by the presence of new surface species in the catalysts after reaction.

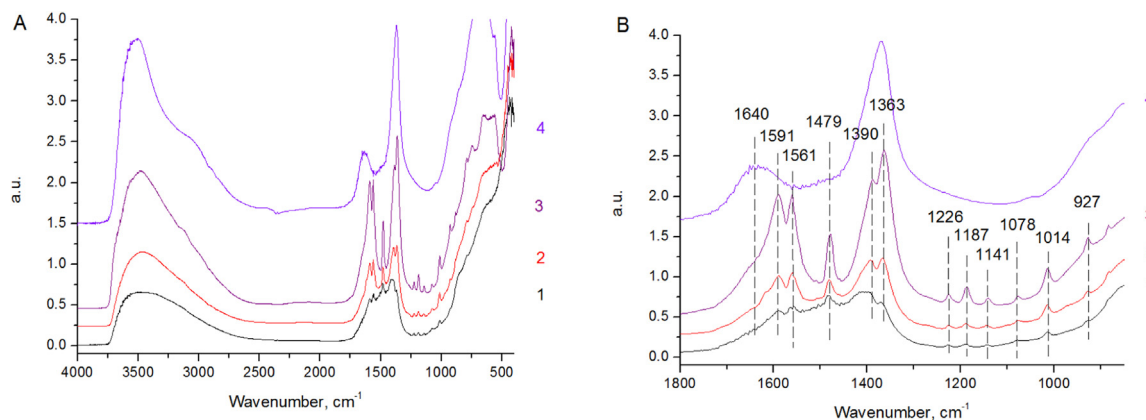
In summary, the characterization data prove that the increase in water content in the aqueous furfural mixture promotes the rehydration of the Mg-Al mixed oxide and facilitates the formation of reconstructed HTC. As soon as Brønsted basic sites are formed in the reconstructed material, its activity in furfural conversion increases as demonstrated by the increase in both F-OH and furoyl furoate yield. After the reaction, the catalyst contains additional species which differ from carbonate or  $\text{OH}^-$  anions as well as from water molecules. Taking into account the concentration of F-OH in the liquid reaction products together with the absence of furoic acid among these products, it is highly probable that these newly formed species found in the catalysts after reaction are surface furoate species. To support this claim, a specific study of furoic acid interaction with the rehydrated catalysts was undertaken.

### 3.4. The study of interaction between rehydrated HTC and furoic acid

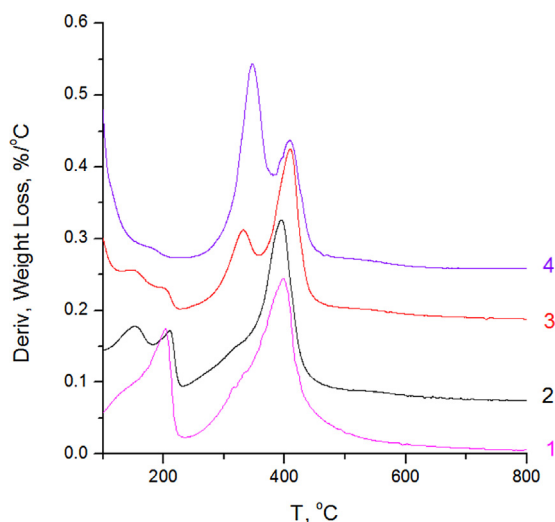
Different amounts of furoic acid were added to the mixture of water and reconstructed HTC after the completion of the rehydration procedure (see the *Experimental*), and the resulting mixture was stirred for 10 min. The solids treated with furoic acid were then separated by filtration using a vacuum pump, dried in  $\text{N}_2$  flow at room temperature and investigated by TGA and DRIFT.

A gradual growth in the DTG signal with the maximum at  $T=330\text{--}340^{\circ}\text{C}$  is observed for rehydrated HTC after its treatment with furoic acid as the ratio of  $m_{\text{FOOH}}/m_{\text{sample}}$  increases from 0 to 0.5 (Fig. 5). The filtrate solution was analyzed by GC, but no furoic acid was detected. This strongly suggests that it was adsorbed on the catalyst and hence the signal at  $T=330\text{--}340^{\circ}\text{C}$  may be unequivocally attributed to the surface furoate species. The position of this signal agrees well with the observed unknown signal in the DTG curves obtained for spent catalysts after their treatment with aqueous furfural mixture (Fig. 3). Consequently, it can be concluded that furoate species are indeed present in the spent rehydrated HTC after Cannizzaro reaction.

Additionally, the observed increase in the signal intensity at  $T=330\text{--}340^{\circ}\text{C}$  is in line with a gradual decrease in the intensity of signals at  $T=200\text{--}210^{\circ}\text{C}$  and  $T=390\text{--}410^{\circ}\text{C}$ . The signal at  $T=200\text{--}210^{\circ}\text{C}$  characterizes interlayer water molecules which are



**Fig. 4.** DRIFT spectra of calcined Mg-Al mixed oxide after its interaction with aqueous furfural mixture in the range of 400–4000  $\text{cm}^{-1}$  (A) and 800–1800  $\text{cm}^{-1}$  (B). 1-HTC-0; 2-HTC-6; 3-HTC-23; 4-reconstructed HTC rehydrated with pure water (reference material).



**Fig. 5.** DTG curves for rehydrated HTC treated with different amounts of Furoic acid.  $m_{\text{FOOH}}/m_{\text{calcinedsample}} = 0$  (1); 0.1 (2); 0.3 (3) and 0.5 (4).

stabilized in interlayer due to hydrogen bonding between them and interlayer compensating anions while the signal at 390–410  $^{\circ}\text{C}$  is characteristic for the removal of structural hydroxyls and compensating anions [12]. The interaction of furoic acid with basic sites and the generation of furoic species should in fact decrease the total amount of structural hydroxyls and compensating anions and thus result in weakened hydrogen bonding between the anions and water molecules. As a consequence, the amount of interlayer water would decrease as would the corresponding signal in DTG data, which is apparent in the experimental data (Fig. 5).

Fig. 6 depicts total DRIFT spectra for rehydrated HTC samples treated with furoic acid in the range of 500–4000  $\text{cm}^{-1}$  (A) and in the specific range of 800–1800  $\text{cm}^{-1}$  (B). The intensity of a shoulder signal at 2700–3200  $\text{cm}^{-1}$  assigned to hydrogen bonding between water molecules and the interlayer anions decreases in intensity with the increase in acid content from 0 to 0.5  $\text{g}_{\text{acid}}/\text{g}_{\text{cat}}$ . (Fig. 6A). The behavior of this band correlates well with the decrease in the intensity of the DTG signal in the range of  $T = 100$ –200  $^{\circ}\text{C}$  and proves the loss of water (including interlayer water) in the samples as a consequence of the formed furoate species. A large difference in the DRIFT spectra between the untreated rehydrated HTC and the samples treated with furoic acid (Fig. 6) is observed in the range of 1300–1700  $\text{cm}^{-1}$ . The peak at 1640  $\text{cm}^{-1}$  attributed to the presence of interlayer water has very low intensity in the spectra of F-OOH-treated rehydrated samples suggesting low water con-

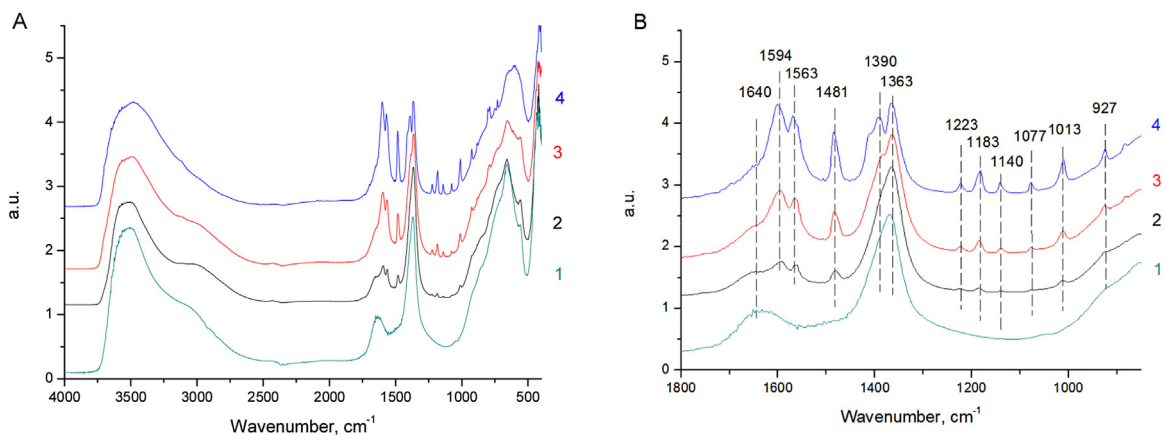
tent in the interlayer. Instead, two peaks appear in this range at 1594 and 1563  $\text{cm}^{-1}$  (Fig. 6B). A peak at 1365  $\text{cm}^{-1}$  which is usually attributed to carbonate cations [12] or, as supposed in the present study, to compensating  $\text{OH}^{-}$ -groups decreases in intensity with the increase in acid content in the mixture while a new band at 1390  $\text{cm}^{-1}$  has appeared. Finally, a very distinctive band at 1481  $\text{cm}^{-1}$  is observed in the samples, and its intensity correlates well with the amount of acid in the treatment solution. In summary, the observed changes and the appearance of new bands in the DRIFT spectra of HTC samples treated with F-OOH can be unequivocally attributed to the surface furoate species formed by adsorption of furoic acid on the basic sites. The formation of furoate species in the treated materials could be also related with the appearance of new small bands in DRIFT spectra in the range of 900–1250  $\text{cm}^{-1}$ . In total, the similarity in the positions of the bands observed in DRIFT spectra of samples either treated with furoic acid or those obtained after reaction with aqueous furfural mixture (Figs. 4 and 6B) allows concluding that the formed surface species on the catalysts are indeed furoates.

### 3.5. Reconstructed HTC as a catalyst for Cannizzaro reaction

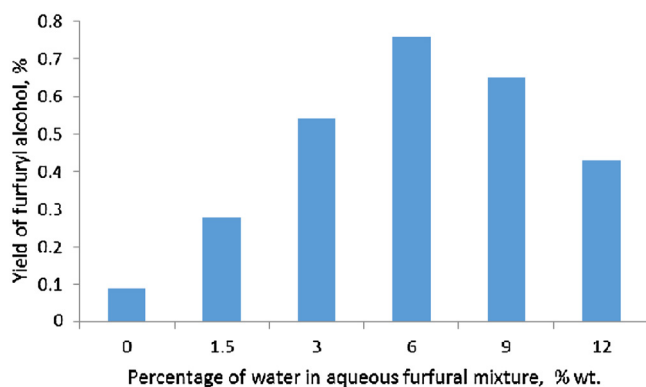
Catalytic results presented above indicate that the increased catalyst activity in CR is observed when reconstructed HTC is formed as a result of complete rehydration of the Mg-Al mixed oxide. This reconstruction is achieved provided large water amount is present in the reaction mixture. On the other hand, the catalytic results indicate that water could have a negative effect on the reaction resulting in a decrease in furfural conversion (Fig. 1). Using a reconstructed HTC prepared by a pre-treatment of mixed oxide with liquid water allows avoiding large water content in the reaction mixture. In addition, these experiments reveal more accurately the effect of water on the course of Cannizzaro reaction, i.e. it allows decoupling the influence of water on catalyst reconstruction (and its activity) from its influence on the reaction.

In these sets of experiments 2 g of freshly calcined HTC was used in rehydration procedure as described in the *Experimental* to prepare reconstructed HTC sample as a catalyst for the reaction. It allows making an accurate comparison between the catalytic activity of mixed oxide and reconstructed samples based on their calcined form. Fig. 7 depicts F-OH yield obtained during the interaction of reconstructed HTC with aqueous furfural mixture. The catalyst possesses poor activity in the conversion of water-free furfural evidencing the necessity of water for the Cannizzaro reaction to take place. In this experiment F-OH yield of  $\sim 0.1$  wt.% could be attributed to the residual water in the dried reconstructed HTC catalyst. Addition of water to furfural promotes





**Fig. 6.** DRIFT spectra of rehydrated HTC treated with different amounts of Furoic acid.  $m_{\text{FOH}}/m_{\text{sample}} = 0$  (1); 0.1 (2); 0.3 (3); 0.5 (4). A – the range of 400–4000  $\text{cm}^{-1}$ , B – the range of 800–1800  $\text{cm}^{-1}$ .



**Fig. 7.** The yield of furfuryl alcohol in experiments with aqueous furfural solution having different water content using dried reconstructed HTC as catalyst. Treac. = 50 °C, t = 3 h,  $m_{\text{cat.}} = 2$  g (calcined base),  $m_{\text{F}} = 30$  g.

the activity of the reconstructed HTC: alcohol yield increases from 0.28 wt.% to 0.76 wt.% as the water content in aqueous furfural mixture grows from 1.5% to 6%, respectively. Nevertheless, further increase in water content in the mixture does not result in a corresponding growth in the furfuryl alcohol yield (Fig. 7). It is worth noting that the maximum F-OH yield observed in experiments with the reconstructed HTC (Fig. 7) is significantly lower than that for Mg-Al mixed oxide (calcined HTC) treated with aqueous reaction mixture (Fig. 1). The observed difference in catalytic behavior suggests that the number of basic sites which are accessible to furfural molecules in the catalyst rehydrated with pure water is lower compared with the catalyst rehydrated *in situ* with biphasic aqueous-organic mixture. Indeed, calculations show that the maximum alcohol yield of 0.76 wt.% produced on reconstructed HTC corresponds to 1.19 mmol of alcohol per 1 g of the catalyst (calcined base). Consequently, 1.19 mmol/g of furoic acid produced by CR is bound with 1.19 mmol/g of basic sites in the catalyst, which is 24.3 wt.% with respect to the bulk Al content. This concentration of basic sites titrated with the acid is much lower than that evaluated from the results of catalytic experiments with Mg-Al mixed oxide. Moreover, it is also slightly lower than that determined by  $\text{CO}_2$ -TPD (1.57 mmol/g, calcined base, Table 1). On the other hand, the concentration of basic sites evaluated in rehydrated HTC by means of Cannizzaro reaction agrees well with the results from [12] that 24.5% of the  $\text{OH}^-$  sites with respect to the bulk Al content in HTC rehydrated in liquid water are evaluated by  $\text{CO}_2$ -TPD. In summary, the obtained catalytic results make us suggest that the concentration of basic sites in the reconstructed HTC depends on

the properties of a liquid medium used for rehydration of Mg-Al mixed oxide, i.e. calcined HTC. Nonetheless, further fundamental studies are necessary to understand the relationship between the basic sites formation and the properties of the media used.

### 3.6. The impact of CR on aldol condensation of furfural and acetone

Aldol condensation (AC) of furfural and acetone takes place in the presence of basic catalysts, for example activated HTC. In general, any of the two components of the reaction mixture interacts with the active centers of the catalyst. Basic sites promote the activation of acetone which is necessary for AC to take place [20,21], while furfural is also transformed by CR, as shown in the present study. Both reactions, AC and CR, proceed simultaneously and share the same active centers; therefore, the deactivation of basic sites with furoic acid formed by CR should influence the conversion of reactants by AC. The following model experiments represent examples aimed to demonstrate the degree of this influence. Three series of catalytic runs with Mg-Al mixed oxide were carried out:

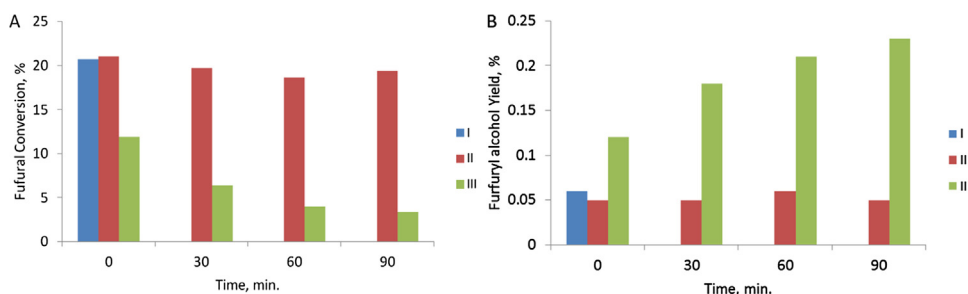
Example I. Mg-Al mixed oxide is added at once to prepared F + Ac mixture (a reference run).

Example II. Mg-Al mixed oxide is initially stirred in acetone for 0–90 min and then furfural is added.

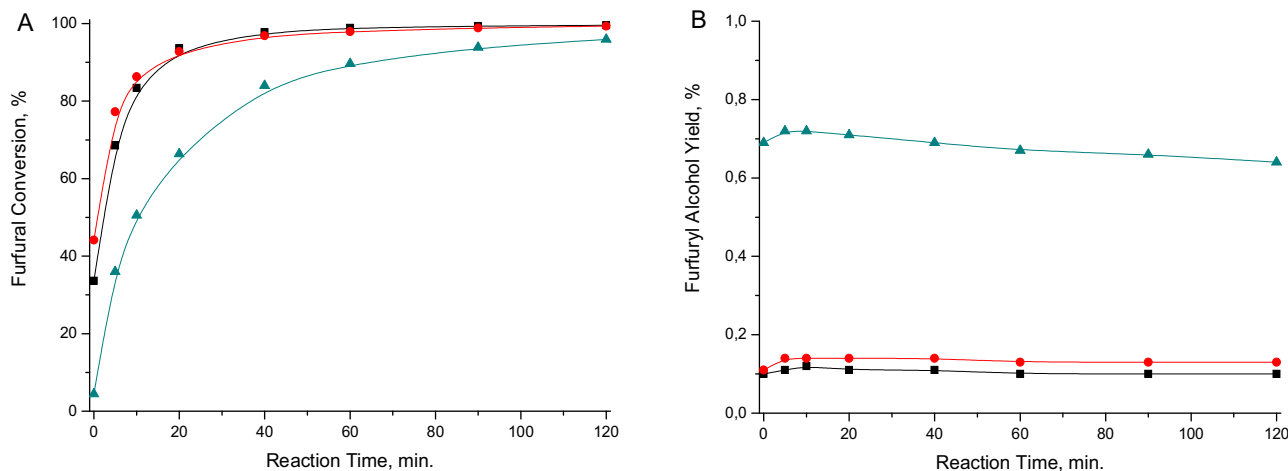
Example III. Mg-Al mixed oxide is initially stirred in furfural for 0–90 min and then acetone is added.

The results of these experiments are presented in Fig. 8. In the reference run (Fig. 8A, Example I) furfural conversion is 20.7% after 3 h of the reaction. Along with compounds formed by aldol condensation, the formation of furfuryl alcohol with the yield of 0.06 wt.% after 3 h is observed. Its presence among other products evidences the simultaneous occurrence of AC and CR, i.e. the formation of furoic acid. As shown above, furoic acid interacts with the basic sites of the catalyst resulting in the formation of surface furoate species. As a consequence, the amount of active sites which are able to participate in both reactions is reduced thus leading to a loss of activity.

The initial stirring of catalyst in acetone for 0, 30, 60 and 90 min, respectively, (Example II) does not introduce any significant effect on its performance in either AC or CR reaction routes. Regardless of the duration of the initial step, the conversion of furfural after 3 h of its addition to the acetone + catalyst mixture is in the range of 18.6–21% while the yield of F-OH is 0.05–0.06 wt.%. These experiments (Example II) evidence that the contact between acetone and catalyst does not contribute to any change in the catalytic activ-



**Fig. 8.** Furfural conversion (A) and the yield of F-OH (B) observed after 3 h of the aldol condensation of furfural and acetone over Mg-Al mixed oxide. I – Catalyst is added to the mixture of acetone and furfural (Reference run); II – Catalyst is stirred in acetone for 0, 30, 60, 90 min followed by furfural addition; III – Catalyst is stirred in furfural for 0, 30, 60, 90 min followed by acetone addition. Reaction conditions:  $m_{\text{cat.}} = 0.5$  g, F:Ac = 6.5/19.7 g/g (1/5 mol/mol),  $T_{\text{reac.}} = 50$  °C.



**Fig. 9.** Furfural conversion (A) and the yield of F-OH (B) observed during the aldol condensation of furfural and acetone over reconstructed HTC. I – Catalyst is added to the mixture of acetone and furfural (Squares); II – Catalyst is stirred in acetone for 30 min followed by furfural addition (Circles); III – Catalyst is stirred in furfural for 30 min followed by acetone addition (Triangles). Reaction conditions:  $m_{\text{cat.}} = 0.5$  g (calcined base), F:Ac = 6.5/19.7 g/g (1/5 mol/mol),  $T_{\text{reac.}} = 25$  °C. Prior to catalyst addition the reaction mixtures (I–III) are mixed with 0.4 g of water to promote CR.

ity in AC, so the behavior of the catalyst is comparable with that observed in the reference run (Example I).

In contrast, the initial stirring of catalyst in furfural (Example III) leads to unique results (Fig. 8A). Even a brief contact between furfural and catalyst decreases the activity of the catalyst in aldol condensation which is evidenced by furfural conversion of 11.9% after 3 h of the reaction (Fig. 6A). When increasing the time of the initial stirring of the catalyst in furfural up to 90 min, a further decrease in furfural conversion in aldol condensation down to 3.4% is observed. Simultaneously with the decline in the overall activity of the catalyst, the increase in the yield of furfuryl alcohol from 0.12 to 0.23 wt.% is observed as the duration of the first stage of the experiment increases from 0 to 90 min, respectively (Fig. 8B). As postulated above, the presence of F-OH indicates that F-OOH is formed because these two compounds are related with each other by the stoichiometry of Cannizzaro reaction. Being produced by Cannizzaro reaction, F-OOH generates surface furoate species by reacting with the basic sites and, consequently, the basic sites become catalytically inactive. It could be also assumed that the organic salts being formed on the catalyst surface would result in selective leaching of the corresponding catalyst components. To evaluate the plausible leaching, we have analyzed the reaction mixture after catalytic experiment (Example III) by ICP. However, we did not detect any traces of Mg or Al in the solution after reaction. It allows concluding that the catalyst is chemically stable and the organic salts, if formed, stay bound on the catalyst surface. Therefore, the decrease in furfural conversion observed in

these experiments (Example III), can be explained by the gradual poisoning of the catalyst with products formed by CR.

Similar experiments investigating the influence of mixing order of reactants during aldol condensation on furfural conversion were performed with reconstructed HTC (Fig. 9). As expected, the activity of the reconstructed HTC in the reaction was higher in comparison with Mg-Al mixed oxide, so to observe any differences in conversion the catalytic experiments were carried out at  $T = 25$  °C

In agreement with the results obtained for Mg-Al mixed oxide, furfural conversion is similar when the rehydrated catalyst is either added to the mixture of acetone and furfural (Example I) or stirred in acetone for 30 min followed by furfural addition (Example II) (Fig. 9A). In contrast, the activity of the reconstructed HTC in aldol condensation is significantly lower when the rehydrated catalyst is initially in contact with furfural (Example III). In all three cases F-OH is detected among reaction products proving the occurrence of CR, as discussed above. Nevertheless, its yield is much lower in Examples I and II being 0.10–0.14 wt.% in comparison with Example III (0.64–0.72 wt.%). These experiments give an additional evidence that CR proceeds simultaneously with AC and definitely influences the performance of a basic catalyst in the latter reaction.

CR may contribute not only to the observed activity of basic catalysts in aldol condensation reaction involving furfural but may also affect re-using of the catalysts. The loss of the activity of hydroxaldehydes and mixed oxides in several successive catalytic runs of condensation reactions has been reported repeatedly. In general, two different deactivation causes have been considered: fouling caused by subsequent aldol condensations and leaching of active

compounds from the catalyst in the aqueous medium [20]. The results presented in this study evidence that other reasons could explain the loss of catalyst activity in condensation reactions, for example, the occurrence of Cannizzaro reaction. Under the real experimental conditions of AC, a catalyst is in contact with both components of the reaction mixture (acetone and furfural) and the reaction is usually carried out in excess of acetone. Therefore, the probability of furfural interacting with basic sites that is necessary for CR to take place is low under high Ac to F molar ratio in reaction mixture. As a consequence, the influence of CR on catalyst performance in AC is not pronounced and conventional solid basic catalysts exhibit good activity in AC. Nevertheless, it is not possible to avoid a contact between furfural and basic sites, so the AC and CR take place simultaneously, as evidenced by the formation of furfuryl alcohol even at conventional reaction conditions (Figs. 8 and 9B, Example I). Even the small contribution of CR would result in the progressive deactivation of the catalyst thus decreasing its activity in AC and making it difficult to recycle/reuse the catalyst without an oxidative regeneration step. Therefore, the optimization of catalytic properties and the determination of optimum reaction conditions to perform AC which would allow reducing the influence of CR on catalyst behavior are important objectives of forthcoming studies.

#### 4. Conclusions

The rehydration of Mg–Al mixed oxide (calcined as-prepared hydrotalcite) using pure water results in the formation of reconstructed hydrotalcite that possesses OH<sup>−</sup> groups rather than carbonates in interlayer as proved by TGA–MS results. The comparison of DRIFT spectra of the as-prepared and the reconstructed materials allowed concluding that these newly formed hydroxyls are characterized by the band at 1370 cm<sup>−1</sup> which is usually considered as a characteristic band of carbonate groups. The results also show that Mg–Al mixed oxide can be successively rehydrated with aqueous furfural mixture resulting in the formation of reconstructed hydrotalcite structure. The amount of water in the mixture influences the rehydration degree and the total reconstruction of the hydrotalcite structure is observed only when using biphasic (water-organic) reaction conditions. The catalytic data allow concluding unequivocally that Brønsted basic sites of the reconstructed HTC catalyze furfural transformation by Cannizzaro reaction. Both furfuryl alcohol and furfuryl furoate formed during the reaction are evidenced by GC analysis. On the contrary, furoic acid is not detected among reaction products by routine GC analysis because it remains adsorbed on the basic sites of the catalyst forming surface furoates. These species can be detected by both TGA (a peak in the range of T = 320 °C) and DRIFT (characteristic band at 1481 cm<sup>−1</sup>) methods. The formation of the surface furoates leads to a gradual catalyst deactivation, as evidenced by the time dependency of furfural conversion and yield of furfuryl alcohol.

The rehydration of Mg–Al mixed oxide (calcined HTC) with aqueous furfural mixture affords a reconstructed HTC possessing a higher amount of basic sites in comparison with a reconstructed HTC prepared by rehydration of the same Mg–Al mixed oxide with pure water. This is demonstrated by the yield of reaction products formed by CR. It can thus be inferred that the rehydration procedure has a significant influence on the basic properties of the resulting reconstructed material.

The performed comparative experiments show that the Cannizzaro reaction also influences aldol condensation of furfural and acetone. The longer is the contact time between furfural molecules and the basic sites of a catalyst, the lower is the furfural conversion

in aldol condensation. Consequently, Cannizzaro reaction would result in the gradual deactivation of the catalyst thus making it difficult to recycle/reuse the catalyst without an oxidative regeneration step.

#### Acknowledgements

The publication is a result of the project reg. No. GA15-21817S which was financially supported by the Czech Science Foundation of the Czech Republic. The project has been integrated into the National Program for Sustainability of the Ministry of Education, Youth and Sports of the Czech Republic through the project Development of the UniCRE Centre, project code LO1606.

#### Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcata.2016.08.007>.

#### References

- [1] J.I. Di Cosimo, V.K. Díez, M. Xu, E. Iglesia, C.R. Apesteguía, *J. Catal.* 178 (1998) 499–510.
- [2] R.K. Allada, A. Navrotsky, H.T. Berbeco, W.H. Casey, *Science* 296 (2002) 721–723.
- [3] A. Corma, S. Iborra, *Adv. Catal.* 49 (2006) 239–302.
- [4] X. Duan, D.G. Evans (Eds.), *Layered Double Hydroxides, Structure and Bonding Series*, vol. 119, Springer, Berlin, 2006.
- [5] D. Tichit, D. Lutic, B. Coq, R. Durand, R. Teissier, *J. Catal.* 219 (2003) 167–175.
- [6] H. Liu, W. Xu, X. Liu, Y. Guo, Y. Guo, G. Lu, Y. Wang, *Kinet. Catal.* 51 (2010) 75–80.
- [7] D.P. Debecker, E.M. Gaigneaux, G. Busca, *Chem. Eur. J.* 15 (2009) 3920–3935.
- [8] A. Corma, S. Iborra, S. Miquel, J. Primo, *J. Catal.* 173 (1998) 315–321.
- [9] Y. Xi, R.J. Davis, *J. Catal.* 254 (2008) 190–197.
- [10] V.K. Díez, C.R. Apesteguía, J.I. Di Cosimo, *J. Catal.* 215 (2003) 220–233.
- [11] D. Tichit, B. Coq, *Cattech* 7 (2003) 206–217.
- [12] S. Abelló, F. Medina, D. Tichit, J. Pérez-Ramírez, J.C. Groen, J.E. Sueiras, P. Salagre, Y. Cesteros, *Chem. Eur. J.* 11 (2005) 728–739.
- [13] D. Tichit, M.N. Bennani, F. Figueras, R. Tessier, J. Kervennal, *Appl. Clay Sci.* 13 (1998) 401–415.
- [14] C. Xu, Y. Gao, X. Liu, R. Xin, Z. Wang, *RSC Adv.* 3 (2013) 793–801.
- [15] K.K. Rao, M. Gravelle, J. Sánchez-Valente, F. Figueras, *J. Catal.* 173 (1998) 115–121.
- [16] B.M. Choudary, M.L. Kantam, C.R.V. Reddy, K.K. Rao, F. Figueras, *J. Mol. Catal. A: Chem.* 146 (1999) 279–284.
- [17] S. Gámez, J.J. González-Cabriales, J.A. Ramírez, G. Garrote, M. Vázquez, *J. Food Eng.* 74 (2006) 78–88.
- [18] T.N. Pham, D. Shi, D.E. Resasco, *Appl. Catal. B* 145 (2014) 10–23.
- [19] C.J. Barrett, J.N. Chheda, G.W. Huber, J.A. Dumesic, *Appl. Catal. B: Environ.* 66 (2006) 111–118.
- [20] L. Faba, E. Díaz, S. Ordóñez, *Appl. Catal. B: Environ.* 113–114 (2012) 201–211.
- [21] S. Abelló, F. Medina, D. Tichit, J. Pérez-Ramírez, J.E. Sueiras, P. Salagre, Y. Cesteros, *Appl. Catal. B: Environ.* 70 (2007) 577–584.
- [22] S. Cannizzaro, *Ann. Chem. Pharm.* 88 (1853) 129–130.
- [23] I. Sádaba, M. Ojeda, R. Mariscal, J.L.G. Fierro, M. López Granados, *Appl. Catal. B: Environ.* 101 (2011) 638–648.
- [24] P.A. Zapata, J. Faria, M. Pilar Ruiz, D.E. Resasco, *Top. Catal.* 55 (2012) 38–52.
- [25] L. Hora, V. Kelbichová, O. Kikhtyanin, O. Bortnovskiy, D. Kubička, *Catal. Today* 223 (2014) 138–147.
- [26] W.V. Evans, M.B. Aylesworth, *Ind. Eng. Chem.* 18 (1926) 24–27.
- [27] A. Morato, C. Alonso, F. Medina, Y. Cesteros, P. Salagre, J.E. Sueiras, D. Tichit, B. Coq, *Appl. Catal. B: Environ.* 32 (2001) 167–179.
- [28] F. Prinetto, G. Ghiotti, P. Graffin, D. Tichit, *Microporous Mesoporous Mater.* 39 (2000) 229–247.
- [29] J.T. Klopogge, R.L. Frost, *Phys. Chem. Chem. Phys.* 1 (1999) 1641–1647.
- [30] F. Prinetto, G. Ghiotti, R. Durand, D. Tichit, *J. Phys. Chem. B* 104 (2000) 11117–11126.
- [31] F. Millange, R.I. Walton, D. O'Hare, *J. Mater. Chem.* 10 (2000) 1713–1720.
- [32] S.K. Sharma, P.A. Parikh, R.V. Jasra, *Appl. Catal. A: Gen.* 386 (2010) 34–42.
- [33] M.D. Ureña-Amate, N.D. Boutarboch, M. del Mar Socías-Viciano, E. González-Pradas, *Appl. Clay Sci.* 52 (2011) 368–373.
- [34] M.F. Beegum, L.U. Kumari, B. Harikumar, H.T. Varghese, C.Y. Panicker, J. Rasanayana, *Chemistry* 1 (2008) 117–124.