

# Using Mg-AI mixed oxide and reconstructed hydrotalcite as basic catalysts for aldol condensation of furfural and cyclohexanone

O. Kikhtyanin, \*<sup>[a][b]</sup> D. Kadlec, <sup>[a]</sup> R. Velvarská, <sup>[a]</sup> and D. Kubička<sup>[b]</sup>

**Abstract:** This study presents results on aldol condensation of furfural and cyclohexanone in presence of Mg-Al hydrotalcite-derived materials as solid basic catalysts at reaction temperature from 25 to 90 °C and cyclohexanone to furfural molar ratio of 1-10. Mg-Al mixed oxide exhibited reasonable activity with furfural conversion of ca. 50% after 180 min of the reaction at T=90 °C. The activity of reconstructed hydrotalcite was much higher with furfural conversion close to 100% at short reaction rate has increased 30-50 times. At similar reaction conditions cyclohexanone self-condensation on HTC-derived catalysts could not compete with aldol condensation because the former reaction was inhibited by produced water. The change in CH/F molar ratio influenced both furfural conversion and product selectivity, higher furfural content in the reaction mixture favored the second condensation step.

## Introduction

The dependence of price and availability of fossil fuels on political and economic events worldwide as well as environmental concerns require the development of economical and energy-efficient processes for the sustainable production of fuels and chemicals.<sup>[1]</sup> Consequently, the production of advanced biofuels is becoming an increasingly actual and urgent task. Among available biomass resources, lignocellulose is the most appropriate long-term alternative to fossil carbon due to its availability and socio-economic acceptability.<sup>[2-5]</sup> Nevertheless, the successful introduction of biofuels on the fuel market is still limited by their cost and the lack of effective methods for their production.<sup>[1,6,7]</sup>

While a plethora of alternatives to conventional road transport fuels has been put forward, including electricity- or hydrogen-fuelled vehicles, such alternatives are not yet available for air transport. In fact, it was suggested that "...no practical alternatives to kerosene-based fuels for commercial jet aircraft for the next several decades".<sup>[8]</sup> Therefore, biomass-derived aviation drop-in fuels meeting the demanding aviation fuel standards are of immense interest.<sup>[9-11]</sup> In this context, a high

[a]	Dr. O. Kikhtyanin, D. Kadlec, R. Velvarská <sup>a</sup>
	Unipetrol Centre of Research and Education (UNICRE),
	Chempark Litvínov,
	436 70 Záluží-Litvínov, Czechia
	E-mail: oleg.kikhtyanin@vscht.cz
[b]	Dr. D. Kubička
	Technopark Kralupy VŠCHT Praha
	(University of Chemistry and Technology Prague),
	Žižkova 7, 278 01 Kralupy nad Vltavou, Czechia

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content of naphthenic hydrocarbons (>25%) and a proper hydrocarbon chain length (C9 – C16) are essential providing a guideline for selecting appropriate biomass-derived feedstocks as well as for fuel synthesis strategies. From the lignocellulosic biomass point of view, it becomes obvious that (i) condensation reactions need to be applied as the monomeric units of the three lignocellulosic polymers have typically between 5 and 9 carbon atoms in the molecule and that (ii) lignin monomeric units should be used to introduce the naphthenic structure into the final fuel molecules.

Aldol condensation, a well-known reaction of organic synthesis which proceeds in the presence of catalysts with either basic or acidic properties, is a versatile tool to produce complex molecules starting from simple aldehydes and ketones. With respect to biomass valorization, aldol condensation of furfural and acetone has been studied in detail as after hydrogenation the reaction products have characteristics of high quality diesel fuel components.<sup>[12-14]</sup> Nonetheless, the resulting linear hydrocarbons would not be suitable for aviation fuels due to their low volumetric energy density and high pour point.<sup>[9-11,15-17]</sup> In contrast, the selective depolymerization of lignin results in a variety of phenolic and aromatic molecules whose cyclic structure can provide the necessary characteristics of potential aviation fuels produced from biomass. To arrive at aviation fuel components, lignin-derived compounds should be processed by one of the following strategies: (i) aldol condensation of shortchain aldehydes with (substituted) cyclic ketones<sup>[18-21]</sup> obtained by partial hydrogenation of phenolics from lignin<sup>[22,23]</sup> or furanics<sup>[24-26]</sup>), or (ii) self-condensation of cyclic ketones<sup>[27-30]</sup>, or (iii) alkylation of lignin-derived aromatics by short chain alcohols.<sup>[31,32]</sup> In addition, some biomass-derived compounds, such as terpenes, have cyclic aliphatic rings and can be directly used as high-density biofuel additives. [15,16]

The conversion of cyclic ketones into bi-cyclic biofuels by self-condensation reaction was reported in presence of homogeneous and heterogeneous catalysts, both acidic and basic,<sup>[27-30]</sup> hydrodeoxygenation.[27] followed by Aldol condensation of cyclic ketones with furanics in presence of NaOH as a basic catalyst in solvent-free<sup>[18]</sup> or aqueous solutions<sup>[19]</sup> followed by hydrogenation of produced compounds<sup>[18]</sup> have been recently shown to be a promising way to get alkylated naphthenic compounds. NaOH was demonstrated<sup>[18]</sup> to be a very good catalyst in solvent-free condensation of cyclopentanone/cyclohexanone and furfural/5hydroxymethyl-furfural, whereas Mg(OH)<sub>2</sub>, Ca(OH)<sub>2</sub> and Na<sub>2</sub>CO<sub>3</sub> were nearly inactive (with conversion <2.0%). This performance was explained by the inability of weak bases to activate cyclopentanone to form carbanion which is necessary for the condensation. Similar results were obtained by Hronec et al. when performing aldol condensation of cyclopentanone and furfural in aqueous solution.<sup>[19]</sup> They found that Na<sub>2</sub>CO<sub>3</sub>, Ca(OH)<sub>2</sub> and MgO-ZrO<sub>2</sub> were less active as catalysts compared

to NaOH and concluded that it was beneficial to conduct the reaction either at higher reaction temperatures (80-100 °C) and low concentration of a base or at lower temperatures (ca. 40 °C) and higher concentration of a base. The above studies suggest that NaOH is a highly effective and the most promising catalyst for aldol condensation of cyclic ketones and furfural. Additionally it was suggested that, in contrast to NaOH solution, the use of solid base catalysts for this aldol condensation may cause technical problem of separation of the solid catalyst from solid reaction product.<sup>[19]</sup> On the other hand, several technical, economic and environmental disadvantages which arise when using homogeneous catalysts have to be also taken into account.<sup>[20,33]</sup> From this point of view, using solid catalysts in aldol condensation with participating cyclopentanone/ cyclohexanone should have substantial benefits over homogeneous ones including minimization of waste streams resulting to reduced costs and environmental burden<sup>[34,35]</sup> and reducing corrosion issues.

Accordingly, catalysts which could compete with NaOH in catalyzing aldol condensation of furfural and cyclic ketones and thus favor the sustainability of the process have been sought intensively. Recent studies evidence that aldol condensation of furfural and cyclic ketones can be successfully performed in presence of heterogeneous catalysts as well. Wang et al.<sup>[21]</sup> performed aldol condensation of cyclopentanone and furfural over solid acid catalysts (ion-exchange resins and zeolites) under solvent-free conditions. Among investigated catalysts, Nafion exhibited the best performance. It showed good stability and did not deactivate during 4 catalytic runs. Meanwhile, a certain amount of humins was formed during the reaction. Ordóñez et al.<sup>[20]</sup> found that, in contrast to results of Hronec et al.,<sup>[19]</sup> Mg-Zr mixed oxide was a promising catalyst for the aqueous phase furfural and cyclopentanone aldol condensation working at mild conditions. They observed almost complete conversion of furfural in 4 hours at T=293-323 K and furfural to cyclopentanone molar ratio of 1. No doubt, studies on finding promising catalytic systems for aldol condensation of furfural and cyclic ketones should be continued and developed to allow sustainable production of naphthenic in the jet fuel range and thereby improving the sustainability of jet fuels.

Mg-Al mixed oxides and hydrotalcite-like materials have been successfully used as catalysts for aldol condensation reactions, mostly with the participation of furfural and/or acetone, under batch<sup>[33,36-39]</sup> as well as flow reaction conditions.<sup>[40]</sup> Asprepared hydrotalcite-like materials (HTC) are solids having structure closely related to that of the mineral hydrotalcite (HTC), that is, rhombohedral Mg<sub>6</sub>Al<sub>2</sub>(OH)<sub>16</sub>CO<sub>3</sub>•4H<sub>2</sub>O. The most known Mg-Al HTC consist of a brucite-like [Mg(OH)2] network wherein isomorphous substitution of Mg2+ ion by Al3+ occurs and the excess positive charge is compensated by gallery anions which are located in the interlayer along with water molecules.<sup>[41-43]</sup> The Mg-Al HTCs can be used as catalysts either in the form of mixed oxides Mg(AI)O with Lewis basicity obtained by calcination of the as-prepared Mg-Al precursor or in the form of reconstructed HTCs with Brønsted basicity as the rehydrated form of these calcined materials.<sup>[44]</sup> It is worth noting a special and constantly growing interest in activated hydrotalcites obtained by rehydration of the mixed oxides for different catalytic applications.<sup>[36,43-45]</sup> Nevertheless, to the present no information can be found in literature on the catalytic performance of either Mg-AI mixed oxides or reconstructed HTCs in aldol condensation of cyclic ketones and furfural.

The aim of this work is to provide deeper understanding of the role of different functionalities in solid base catalysts derived from hydrotalcites in condensation reactions of cyclic ketones with aldehydes derived from biomass. Specifically, this work is focused on cyclohexanone self-condensation and furfuralcyclohexanone aldol condensation over an Mg-Al mixed oxide and a reconstructed HTC. The effects of reaction conditions as well as different basicity of the catalysts on their activity and selectivity in both reactions are described. Additionally, re-using of the catalysts in consecutive aldol condensation runs, which is vital from the sustainability point of view, is presented as well. Although relying on established raw materials and known catalytic systems, the presented original results shed light on some of the transformation peculiarities and demonstrate their unique potential to succeed in the guest for efficient upgrading of renewable aldehydes and ketones into a feedstock for aviation fuels production ...

## **Results and Discussion**

The Mg-Al hydrotalcite-derived catalysts used for aldol condensation of furfural and cyclohexanone have been investigated previously<sup>[36,46]</sup> and thus, for the sake of conciseness, their detailed physico-chemical characterization is included in the Supporting Information (see Table S1 and Figures S1-S5 in the *SI*).

Both F and CH aldol condensation and CH selfcondensation proceed simultaneously under the contact of F and CH mixture with Mg-AI mixed oxide or reconstructed hydrotalcite. A large consumption of CH by self-condensation reaction route could influence the results obtained in F and CH aldol condensation. Besides, CH self-condensation can afford products that could also be further upgraded to aviation fuel components. Consequently, this reaction was studied separately by varying the type of catalyst and reaction conditions.

#### Cyclohexanone self-condensation

Cyclohexanone self-condensation is a reversible reaction<sup>[28,29]</sup> that can be catalysed by acidic<sup>[28,47,48]</sup> or basic catalysts.<sup>[27,29]</sup> According to the accepted reaction route (Scheme 1 <sup>[28,29]</sup>, the adduct 'hydroxy -[1,1'-bicyclohexyl]-2-one (D1) is formed first and then dehydrated in situ, yielding an isomeric mixture of reaction products, namely, 2-(1-cyclohexen-1-yl)cyclohexanone (D2) and 2-cyclohexylidencyclohexanone (D3).

The conversion of cyclohexanone over the as-prepared HTC with no pronounced basicity increased with the growth of reaction temperature but did not exceed 3% at 90°C after 3 hours of the experiment (Figure 1). The activity of both Mg-Al mixed oxide and reconstructed HTC was considerably larger proving the base-catalysed character of this reaction. The observed catalytic performance of these catalysts would suggest



Scheme 1. The reaction pathway of cyclohexanone self-condensation.<sup>[28]</sup>

that both Lewis basic sites in the Mg-Al mixed oxide and Brønsted basic sites in the reconstructed HTC are responsible for the reaction. Nevertheless, Tichit et al.<sup>[37]</sup> suggested that the pre-adsorption of water in a suitable amount on the surface of MgO or Mg-Al mixed oxide transforms the Lewis basic sites into active hydroxyl groups (Brønsted basic sites) and increases the activity of the catalysts in acetone self-condensation, while a very high water amount inhibited the reaction.<sup>[37]</sup> The high complexity of the reaction system due to the thermodynamic equilibrium and water inhibition effects prevents unequivocal determination of the active basic sites. Nonetheless, it is clear that Brønsted basic sites are active in the reaction.

For both catalysts, Mg-AI mixed oxide and reconstructed HTC the interpretation of the obtained results is not straightforward as CH conversion over both the catalysts did not increase with the increase of reaction temperature. In contrast, Liang et al.<sup>[30]</sup> investigated cyclopentanone self-condensation over Mg-Zr mixed oxide and observed a sharp increase in conversion with the growth of reaction temperature. A careful comparison of CH conversion over the tested catalysts shows that there is a limiting value of ca. 3-4% conversion at 90 °C in the case of Mg-AI mixed oxide and reconstructed HTC (Figure 1). This would suggest that the reaction is either thermodynamically limited or severely inhibited by water and higher conversions can be achieved only in absence of water.

Such behaviour can be supported, by analogy, by results on self-condensation of acetone to diacetone alcohol (DAA), which is a reversible reaction and the equilibrium concentration of DAA decreases with increasing temperature.[49] Assuming a similar mechanism for both acetone and cyclohexanone selfcondensation in presence of basic catalysts, the decrease of cyclohexanone conversion with increasing temperature is thus not surprising. Further, the hypothesis on the inhibiting effect of water is corroborated by the product distributions. As D1 is always the major condensation product, due to the limited dehydration strength of the studied catalysts, the ratio of dehydrated to non-dehydrated products, i.e. (D2+D3)/D1, is used as a measure expressing presence of water in the products (Figure 2). It is clearly seen that regardless the reaction temperature, the highest conversion is achieved when the (D2+D3)/D1 remained 0. As the ratio (D2+D3)/D1 increased to ca. 0.03 - 0.05, i.e. water was formed by dehydration (this corresponds to about 3 to 5% selectivity to dehydration products), the conversion remained constant. This allows concluding that indeed water formation has a strong inhibiting effect on the CH self-condensation. First, it prevents the formation of enolate ion due to interaction of cyclohexanone with basic hydroxyl group on the surface of a catalyst. Second, water can reduce the production rate of dehydrated products D2 and D3. A similar conclusion was made when considering the kinetics of mesityl oxide formation in acetone selfcondensation.[49] Consequently, it may be expected that an increase in cyclohexanone conversion can be achieved by removing water from the reaction mixture.



Figure 1. The influence of reaction temperature on cyclohexanone conversion over as-prepared HTC (A), Mg-Al mixed oxide (B) and reconstructed HTC (C). 1 - 25 °C, 2 - 50 °C, 3 - 90 °C.

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Figure 2. (D2+D3)/D1 ratio observed in experiments on cyclohexanone self-condensation on Mg-AI mixed oxide (A) and reconstructed HTC (B) at different reaction temperatures. 1 - 25 °C, 2 - 50 °C, 3 - 90 °C.

The above conclusions are further supported by the results of a study using NaOH as a basic catalyst where it was suggested<sup>[29]</sup> that CH self-condensation did not take place at temperatures lower than 100 °C. According to a proposed kinetic model,<sup>[29]</sup> water caused a remarkable decrease in the maximum conversion reachable, due to the growing extent of the reverse reaction with increasing water concentration in the reaction mixture. Thus, it was concluded that the content of water in the media was a key parameter to control the desired cyclohexanone conversion.<sup>[29]</sup> The high conversions reported previously for Amberlyst-15 as an acidic catalyst in the range of 30-60% at T=70-110 °C<sup>[28,48]</sup> contradict the current findings only seemingly. These experiments were conducted either at low reaction pressure or in a flow system and accumulation of water in the reaction mixture was thus avoided. The inhibiting effect of water was also found in the study for cyclohexanone selfcondensation in presence of ion-exchange resin.[47]

The results also indicate that Mg-Al mixed oxide is more active in CH self-condensation compared to reconstructed HTC. The presence of water in the reaction mixture seems to be the crucial factor determining the activity of both Mg-Al mixed oxide and reconstructed HTC in the reaction. The slightly better performance of the mixed oxide catalyst could be attributed to the possibility of its reconstruction to HTC which consumes part of the water formed during the dehydration of D1.

The negative effect of water on the catalyst behaviour of the reconstructed Mg-Al HTC was proved by experiments in which water was either added to or removed from the reaction mixture. Figure 3A demonstrates that water added to CH obviously reduced the conversion of CH on the reconstructed HTC at T=25 and 50 °C from 5.1 to 3.6% and from 8.1 to 3.9%, correspondingly, while at T=90 °C CH conversion (ca. 3.1%) did not change since at these reaction conditions water was formed abundantly by dehydration of the primary D1 product.



Figure 3. The catalytic performance of reconstructed HTC in converting pure cyclohexanone and its aqueous (5% of water) solution (A). Cyclohexanone conversion in experiments with water separation from reaction mixture (B). Reaction time – 180 min.

On the other hand, the removal of water from the reaction mixture (by performing the reaction at T=90-150 °C without a cooler-condenser above the glass reactor and thus favouring water evaporation during the reaction) had a positive effect on the activity of the reconstructed HTC. This is obvious already at T=90 °C; when water could evaporate (i.e. was not condensed), CH conversion increased from 3.1 to 7.3% (Figure 3B). The growth in reaction temperature subsequently resulted in an increased activity of the reconstructed HTC, so that CH conversion attained 44% at T=150 °C.

The results obtained during the study of CH selfcondensation in presence of Mg-Al mixed oxide and reconstructed HTC allow making the following conclusions. First, the different nature of basic sites had only a small impact on the performance of the two catalysts in cyclohexanone selfcondensation. Second, an increase in the reaction temperature promoted the increase in CH conversion only to a certain extent, possibly due to thermodynamic limitations. At the same time the growth of reaction temperature increased the extent of dehydration of the intermediate aldol. Consequently, the formed water inhibited the catalyst activity and/or promoted the reverse reaction (retro-aldolization) leading ultimately to a lower CH conversion at 90°C than at 25°C. In other words, cvclohexanone conversion by self-condensation on the Mg-Al mixed oxide and the reconstructed HTC is very low at increased reaction temperatures when water is present in the reaction mixture. These results should be kept in mind when discussing results on aldol condensation of furfural and cyclohexanone.

#### Aldol condensation of furfural and cyclohexanone

A special experiment on F and CH aldol condensation in absence of a catalyst confirmed no any reaction occurred (furfural conversion was below 0.1% at T=90 °C after 3 hours). Introducing a catalyst into the reaction mixture initiated the reaction and resulted in the formation of several products. To identify them, a reaction mixture was analysed by GC-MS. Based on the identification the following reaction network is proposed (Scheme 2). It is worth noting that more than one compound with the same molecular weight was determined by GC-MS. Similar observation was reported<sup>[20]</sup> and peaks belonging to compounds with the same number of carbon atoms were attributed to cis and trans isomers of the same molecule. By analogy with the results from<sup>[20]</sup> all products with the same molecular weight were considered together in all GC analyses as a single compound.

It is worth noting that the conversion of cyclohexanone by self-condensation did not exceed 2% in all experiments on F+CH aldol condensation. The absence of the cyclopentanone self-condensation adducts during aldol condensation of furfural and cyclopentanone was also suggested.<sup>[20]</sup> As shown above, this can be explained by the formation of water by the dehydration of an aldol (FCH-OH) which is the primary product of aldol condensation of furfural and cyclohexanone. Being formed, water favours retro-aldolization in cyclohexanone self-condensation route. Accordingly, this reaction was excluded from the consideration of catalytic results on aldol condensation because of its negligible impact.

The effect of catalyst type and reaction temperature on furfural conversion and the composition of products obtained in aldol condensation of furfural and cyclohexanone were studied at CH/F molar ratio of 5. This choice was dictated by the formation of a yellow solid product in experiments with high furfural content. Similar observations were reported in other studies.<sup>[18-20]</sup> After separation from the reaction mixture, this solid product was dissolved in excessive benzene and analysed by GC-MS which proved that it consisted mainly of F<sub>2</sub>CH. Its formation disrupted the homogeneity of the reaction mixture and made it difficult (if possible) to periodically withdraw liquid samples to analyse the composition of the reaction products in dependence on reaction time. All experiments on the effect of reaction temperature and catalyst type with periodic sampling were therefore carried out at a high CH/F molar ratio of 5, which prevented the excessive occurrence of the second step of aldol condensation to form F2CH. The used CH/F molar ratio additionally promoted the homogeneity of the reaction mixture by dissolving aldol condensation products in excessive cyclohexanone. It also allowed obtaining carbon balance values of ≥90% in all experiments, suggesting a small contribution of side reactions or of the excessive formation of oligomers by consecutive condensation steps.

Three Mg-Al-derived catalysts were investigated in F and CH aldol condensation: (i) as prepared Mg-Al hydrotalcite, (ii) Mg-Al mixed oxide obtained by calcination of as prepared hydrotalcite at T=450 °C and (iii) reconstructed hydrotalcite obtained by liquid phase rehydration of the Mg-Al mixed oxide. Among them, the as-prepared hydrotalcite showed very low activity; furfural conversion reached less than 3% after 3 hours at 90 °C. Thus, in the following discussion only the performance of the Mg-Al mixed oxide and the reconstructed HTC is considered. It also proves that thermal activation of the Mg-Al hydrotalcites before their use as catalysts is essential.



Scheme 2. The reaction pathway of aldol condensation of furfural and cyclohexanone.



Figure 4. Furfural conversion in aldol condensation of furfural and cyclohexanone (CH/F molar ratio = 5) as a function of reaction time at 25, 50 and 90 °C over Mg-Al mixed oxide (A) and reconstructed Mg-Al HTC (B).

The conversion of furfural over Mg-Al mixed oxide and Mg-Al reconstructed HTC as a function of reaction time at three reaction temperatures (25, 50 and 90 °C) and constant feed composition (cyclohexanone/furfural molar ratio = 5) is shown in Figure 4. The conversion of furfural over Mg-Al mixed oxide increased from 7.1% to 51.9 % after 180 min. of the reaction with the growth of reaction temperature from 25 °C to 90 °C. The catalytic activity increased dramatically when Mg-Al mixed oxide was rehydrated to form reconstructed Mg-Al HTC with furfural conversion close to 100% already after 60 min. of the reaction. It could not be explained by the differences in the textural properties of Mg-Al mixed oxide and reconstructed HTC, because BET surface areas of these catalysts were 180 and 43 m<sup>2</sup>/g, respectively (see the SI). Although Mg-Al had larger surface area than the reconstructed HTC, it exhibited lower activity in the reaction. Accordingly, the increase in the catalytic activity demonstrates that by reconstruction of HTC structure suitable active sites are formed, namely the Lewis basic sites are converted into the more active Brønsted basic sites. The increase in the activity was quantified by estimating the initial reaction rate over Mg-Al mixed oxide and reconstructed HTC catalysts, respectively (Table 1). Depending on the reaction temperature, the initial reaction rate over the reconstructed Mg-Al HTC is 30 to 50 higher than that over the Mg-Al mixed oxide. It is noteworthy that complete conversion of furfural was not attained even after 3 hours which contrasts with aldol condensation of furfural and acetone at similar reaction conditions.[36]

 Table 1. Initial catalytic activity of Mg-Al mixed oxide and reconstructed Mg-Al

 HTC in aldol condensation of furfural and cyclohexanone (CH/F molar ratio = 5).

Temperature, °C	r <sub>in.</sub> (MO), mmol/(g∙min)	r <sub>in.</sub> (HTC), mmol/(g∙min)	r <sub>in.</sub> (HTC)/ r <sub>in.</sub> (MO)
25	0.3	9.7	32.3
50	0.7	28.2	40.3
90	1.7	86	50.6

Figure 5 depicts a change in the composition of reaction products observed on Mg-Al mixed oxide and reconstructed HTC in dependence on F conversion at different reaction temperatures. According to the suggested reaction scheme (Scheme 2), aldol (FCH-OH) is the initial product formed by the condensation of furfural and cyclohexanone. Indeed, its selectivity on Mg-Al mixed oxide is close to 100% at low F conversion (Figure 5A1). The increase in reaction temperature favours FCH-OH dehydration as evidenced from the increase in selectivity to FCH (Fig. 5B1) and F<sub>2</sub>CH (Fig. 5C1) at similar conversion levels. Selectivity to FCH-OH decreases (and, accordingly, selectivity to FCH and F<sub>2</sub>CH increase) very fast at the beginning of the reaction at F conversion below 10% followed by a steady-state region. The observed change in the composition of the reaction products allows suggesting that the properties of Mg-Al mixed oxide are modified in the course of the reaction as discussed further.

Similar to experiments with Mg-Al mixed oxide, the increase of reaction temperature in experiments with reconstructed HTC facilitates FCH-OH dehydration to FCH and the formation of the second condensation product (F<sub>2</sub>CH). The intermediate aldol (FCH-OH) is the most abundant reaction product at T=25 and 50 °C and F conversion below 80% (Figure 5A2), but the changes in selectivity with increasing F conversion are rather peculiar. At T=25 °C, the initial FCH-OH selectivity is 71.5%; it increases to 89.7% at furfural conversion≈30% followed by a small decrease to 84.9% with increasing F conversion. At higher reaction temperatures (T=50 °C and 90 °C), FCH-OH selectivity shows more common trend for an intermediate reaction product: it monotonously decreases with the increasing F conversion. Finally, as F conversion is approaching 100%, a sharp drop in FCH-OH selectivity is

The change in selectivity to FCH observed on the reconstructed HTC exhibits an opposite trend to that observed for FCH-OH which is in accordance with the reaction route (Scheme 2). In general, the lower the selectivity to FCH-OH, the higher the selectivity to dehydrated FCH, and vice versa. At

observed in all experiments (Figure 5A2).

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Figure 5. Selectivity to FCH-OH (A), FCH (B) and F<sub>2</sub>CH (C) observed in aldol condensation of furfural and cyclohexanone over Mg-Al mixed oxide (left) and reconstructed HTC (right). T=25 °C(1), 50 °C(2) and 90 °C(3). CH/F molar ratio = 5.

T=25 °C, the initial selectivity to FCH shows a notable decrease from 21.5 to 8.3% at the beginning of the reaction, a steady-state behaviour in the range of F conversion between 30 and 80% and a sharp increase at higher F conversion (Figure 5B2). In contrast, at 50 °C and 90 °C the constant increase in selectivity to FCH during all the experiments is observed. The change in the selectivity to F2CH follows the same trend as observed for FCH, i.e. a complex behaviour at T=25 °C and a slight increase at higher reaction temperatures (Figure 5C2). The absence of a sharp increase in F<sub>2</sub>CH selectivity at T=50 and 90 °C at the end of experiments is probably concerned with the lack of furfural molecules available for the second condensation step at high conversion levels.

The selectivity to FCH at approximately the same conversion shown for both catalysts at each reaction temperature studied (Figure 6) indicates that indeed the dehydration performance of the reconstructed Mg-Al HTC is considerably better than that of Mg-Al mixed oxide. It can thus be inferred that the active sites in reconstructed HTC are intrinsically more active in dehydration than the sites in Mg-Al mixed oxide. However, there are some peculiarities observed in the product distribution when approaching complete furfural conversion (Figure 5), namely there is a sharp decrease in the selectivity to the FCH-OH accompanied by a sharp increase in



Figure 6. Selectivity to FCH at 25, 50 and 90  $^{\circ}$ C over Mg-Al mixed oxide (F conversions 7, 18 and 52%, respectively) and reconstructed Mg-Al HTC (F conversions 8, 20 and 63%, respectively) in aldol condensation of furfural and cyclohexanone (CH/F molar ratio = 5).

the selectivity to its dehydration product, i.e. FCH. Such behaviour suggests that, when nearly all furfural is consumed, more active sites become available for the dehydration step. This could be a consequence either of competitive adsorption of furfural and FCH-OH on the basic sites (with furfural being preferentially adsorbed) or of recovery/regeneration of some active sites.

Detailed analysis of the product distribution provided evidence supporting the second hypothesis. It was shown that aldol condensation of furfural and acetone is affected by Cannizzaro reaction that yields furoic acid and furfuryl alcohol.<sup>[50]</sup> While furoic acid interacts with the basic sites of reconstructed HTC, presumably with interlayer hydroxyls, forming interlayer furoates and is thus not seen among the reaction products, furfuryl alcohol can be detected. The amount of furfuryl alcohol depends, among other factors, on the reaction rate of aldol condensation of furfural and cyclohexanone, as this is a faster reaction consuming furfural in the reaction mixture. Hence, often the concentration of furfuryl alcohol in the reaction products is close to its detection limit. Nonetheless, in an experiment over reconstructed HTC at T=25 °C, furfuryl alcohol was reliably detected and its yield is plotted as a function of the reaction time in Figure 7.

It is surprising to see that the yield of furfuryl alcohol passes through a maximum and decreases as furfural conversion approaches to 100%. Simultaneously, at furfural conversion ≥50% the formation of furfuryl ester of the furoic acid is observed (Figure 7). The occurrence of this compound among reaction products indicates the interaction of furfuryl alcohol with furoate species which are present in the interlayer of the spent catalyst. It follows that when furoic acid is consumed in the esterification reaction, some basic active sites become again available for other reactions. Judging by the peculiar selectivity profiles at near complete furfural conversion (Figure 5), dehydration of FCH-OH to FCH is one of them.



**Figure 7.** Furfuryl alcohol (F-OH) and furfuryl furoate (FOOF) yields observed during aldol condensation of furfural and cyclohexanone over reconstructed HTC (T= $25 \,^{\circ}$ C, CH/F molar ratio = 5).

The results strongly suggest that aldol condensation of furfural and cyclohexanone is affected by deactivation due to the formation of furoic acid by Cannizzaro reaction from furfural, so two further aspects have been studied: reusing of the spent catalyst in several reaction cycles and the influence of CH/F molar ratio.

#### **Reusing of the reconstructed HTC**

The performance of the reconstructed HTC used in three consecutive catalytic runs at T=25 °C with an intermediate catalyst separation by simple filtration (i.e. without any additional steps, like washing, calcination, etc.) is presented in Figure 8. The conversion of furfural dropped first moderately from 97% at the end of the first run to 88% after the second run. At the end of the third run, the decline of furfural conversion was already substantial and furfural conversion reached just 36% (Figure 8A). This was accompanied by a dramatic decrease in the yield of furfuryl alcohol (Figure 8B) that is an indication of the occurrence of Cannizzaro reaction and, hence, furoic acid formation. Such a progressive loss of catalyst activity observed in consecutive runs is unequivocally concerned with a decrease in the amount of accessible active sites. In general, two different deactivation causes have been considered: the fouling of the catalyst surface with reaction products and the leaching of active compounds from the catalyst into the reaction mixture.[39] We could exclude leaching since the catalyst composition (Mg, Al) did not change after catalytic run, Mg nor Al were found in the liquid phase (as it was evidenced by ICP analysis) and after removing catalyst from the reaction mixture no further aldol condensation reaction was observed. Therefore, the spent catalysts after the first and the third cycle were analysed by TGA and FTIR and the results were compared with those obtained for the fresh catalyst.

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Figure 8. Furfural conversion (A) and yield of furfuryl alcohol (B) observed on reconstructed HTC in three consecutive catalytic runs. T = 25 °C, CH/F=5, time - 60 min.

The weight loss of the fresh reconstructed HTC was 43.8% and it increased to 51.8-52% for the spent catalysts after the first and the third catalytic runs (Figure 9A). TGA curves also showed that the weight loss of the spent catalysts continued to grow at temperatures as high as 800 °C, in contrast to the freshly reconstructed HTC. The increase in the weight loss at temperature above ≈500 °C can be attributed to heavy deposits formed in the reaction, plausibly heavy aldol condensation products that were reported previously.<sup>[40]</sup> The comparison of TGA results presented in Figure 9A suggests that the total weight loss of catalysts after either single or three catalytic runs was very similar. It means that in consecutive catalytic runs most of the heavy reaction products were formed already after the first experiment with no further accumulation of these compounds in the subsequent runs. Nonetheless, this contradicts to the steep decline in furfural conversion between the second and the third run. The yield of furfuryl alcohol (Figure 8B), on the other hand, suggests that in the second run still a significant amount of furoic acid and thus interlayer furoates was formed, while in the third run it was significantly reduced. Consequently, it can be concluded that deactivation by furoic acid that interacts with the Brønsted basic sites forming interlayer furoate species is responsible for the significant drop in the catalyst activity. Figure 9B evidences the presence of a shoulder signal in the range of T=310-350 °C on DTG curve after the third run. This signal was previously attributed to decomposition of furoates.<sup>[50]</sup>

DRIFT spectrum of the spent catalyst after catalytic runs, both the first and the third, shows the appearance of new bands compared to those observed in the spectrum of the fresh reconstructed HTC (see the *SI*, Figure S5). These were previously ascribed to furoates.<sup>[50]</sup> Thus, both the TGA/DTG and DRIFT results support catalytic data and evidence the formation of interlayer furoates which are formed in reconstructed HTC during aldol condensation of furfural and cydohexanone. The formation of these species results in a decline of catalyst activity. As evidenced by TGA data, these furoates can be decomposed thermally.





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Besides the accumulation of heavy deposits and the occurrence of Cannizzaro reaction, there could be also other plausible causes of the observed decrease in the activity of the reconstructed HTC in the recycling experiments. Aldol condensation on reconstructed hydrotalcites occurs with the participation of active OH-groups which are located near the edges of the platelets.<sup>[45]</sup> These groups are charge-compensating, so their properties, in terms of both basic strength and concentration, should be very sensitive to small changes in the surface properties of HTC platelets. Mechanisms of deactivation, such as surface reconstruction, pore collapse, or the destruction of the crystalline structure, which may occur during sequential catalytic runs cannot be excluded; however, this is outside the scope of the present study.

#### Influence of CH/F molar ratio

The results on the influence of cyclohexanone to furfural molar ratio in the range from 1 to 10 over the reconstructed Mg-Al HTC at 25 and 90  $^\circ$ C are shown in Figure 10. At both reaction

temperatures, furfural conversion observed after 180 min. gradually increased with the growth in CH/F ratio (Figures 10A and B). This increase is more pronounced at 25 °C what could be concerned with the effect of Cannizzaro reaction rather than the change in feed composition itself since the furfural-tocatalyst ratio was kept constant. Indeed, as Cannizzaro reaction is a bimolecular reaction of two furfural molecules, its probability increases with the increasing concentration of furfural in the reaction mixture. The deactivation caused by furoic acid is then augmented and consequently the conversion of furfural is lower. Due to the lower reaction rate of aldol condensation at 25 °C the effect of Cannizzaro reaction is more pronounced at this temperature (Figure 10A). The conclusion is further corroborated by the yield of furfuryl alcohol in the reaction products that increases with the increasing CH/F molar ratio (see the SI, Figure S6) and by the analysis of spent catalysts by TGA and DRIFT that confirmed increased abundance of furoates on the spent catalyst at lower CH/F molar ratio (see the SI, Figure S7).



Figure 10. The influence of CH/F molar ratio on F conversion observed on reconstructed HTC after 180 min. of the reaction at T=25 °C (A) and after 40 min. of the reaction at T=90 °C (B). The composition of reaction products at T=25 °C (C) and 90 °C (D) at furfural conversion of ≈50%.

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The composition of the reaction products as a function of the CH/F molar ratio was compared at nearly equal furfural conversion of ≈50% for both temperatures (Figures 10C and D). In all experiments at T=25 °C, the intermediate aldol FCH-OH was the most abundant reaction product and its selectivity decreased from 94 to 85% when increasing the CH/F molar ratio from 1 to 10 (Figure 10C). At the same time, the selectivity to dehydrated FCH increased from 3 to 13% (Figure 10C). It can be inferred that the dehydration performance of the reconstructed Mg-Al HTC is improved at lower furfural concentration in the reaction mixture, possibly due to the diminished extent of Cannizzaro reaction. Similarly, at 90 °C the selectivity to FCH also increased (from 28 to 49%) with the increasing CH/F ratio (Figure 10D). On the contrary, the selectivity to F<sub>2</sub>CH decreased from 36 to 10% upon increasing the CH/F molar ratio from 1 to 10 (Figure 10D) which can be attributed to the limited availability of furfural for the second aldol condensation step, i.e. for the reaction between FCH and F. at high CH/F molar ratios.

The presented results evidence that, by varying CH/F molar ratio, it is possible to influence the composition of obtained products. At a relatively high CH/F molar ratio (using CH excess) FCH-OH and FCH are predominantly formed, both having 11 carbon atoms, which fits well in the composition range of jet fuels. On the other hand, high furfural contents should be used if the production of F<sub>2</sub>CH, i.e. the product with 16 carbon atoms, is targeted. In both cases, HTC-derived catalysts show promising performance in aldol condensation of furfural and cyclohexanone that can be produced by the complex processing of lignocellulosic biomass. Nevertheless, the high activity of reconstructed HTC in the reaction is accompanied by the deactivation of the catalyst, what is evidenced by experiments with consecutive catalytic runs (Figure 8). The formation of compounds that block the active sites of the catalyst is a key factor that can influence the successful development of this environmentally-friendly way of producing bio-derived jet fuel. Consequently, the improvement of the properties of a solid base catalyst and the optimization of reaction conditions are considered as a challenge for forthcoming studies.

## Conclusions

The results of this study evidence that both Mg-Al mixed oxide and reconstructed HTC produced from an as-prepared HTC using corresponding treatments (thermal activation and rehydration), can be used as catalysts for valorisation of cyclic ketones and furanics by aldol condensation. The performance of both basic catalysts in cyclohexanone self-condensation is very sensitive to moisture in the reaction mixture. Water either initially present in the feed or formed by dehydration of the produced intermediate (D1) decreases cyclohexanone conversion. Nevertheless, if water is constantly removed from a reactor, cyclohexanone conversion substantially increases up to 44% at 150 °C. Consequently, CH self-condensation does compete only to a very minor extent with the aldol condensation of CH and F.

The activity of the reconstructed HTC in aldol condensation of furfural and cyclohexanone is significantly higher than that of the Mg-Al mixed oxide, confirming that Brønsted basic sites rather than Lewis basic sites are responsible for the catalyst activity, similar to other aldol condensations. The reaction between furfural and cyclohexanone on reconstructed HTC proceeds at a high reaction rate even at T=25 °C. The increase in the reaction temperature promotes both the dehydration of the intermediate aldol to FCH and the second condensation step to F2CH. In addition, the ratio between FCH and F<sub>2</sub>CH reaction products may be changed by varying the molar ratio between furfural and cyclohexanone in the reaction mixture. The observed high conversions of the reactants together with the possibility to regulate the composition (molecular weight) of the reaction products hold substantial potential for the development of a reliable process aiming to produce bio-derived naphthenic components of jet fuel. Currently, the catalyst deactivation by side-products adsorbed on the catalysts surface poses the key challenge that needs to be further addressed. As shown in this study, it may be partially overcome by optimization of reaction parameters, e.g. the cyclohexanone/furfural molar ratio. Gentle catalyst regeneration is another alternative to be further investigated.

## **Experimental Section**

#### Catalyst

The details of Mg-Al HTC (Mg/Al=3) preparation are presented elsewhere.<sup>[33]</sup> Briefly, the sample was synthesized by co-precipitation of an aqueous solution of magnesium and aluminum nitrates with a basic solution of potassium carbonate and potassium hydroxide at constant pH value of 9.5 and T=60 °C. Mg-Al mixed oxide was prepared by calcination of a dried as-prepared HTC (Mg/Al=3) at 450 °C for 3 h. Reconstructed HTC was obtained by rehydration of the mixed oxide in pure water for 10 minutes followed by filtration and drying for 20 minutes using the method described elsewhere.<sup>[36]</sup>

#### Characterization

The structure of catalysts used in the study was confirmed by Xray powder diffraction using a Philips MPD 1880 instrument with CuK<sub>a</sub> irradiation ( $\lambda$  = 0.154 nm) in the 20 range of 5°–70° at the 20 scanning rate of 2.4°/min. Thermogravimetric analysis (TGA/DTG) 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 using the same TGA unit equipped with a mass-spectrometer OmniStar GSD 320 (Pfeiffer-Vacuum) with a MID (Multiple Ion Detection) measurement mode, a SEM (Secondary Electron Multiplier) detector and a quadrupole mass analyzer. DRIFT spectra were recorded on a Nicolet IS 10 FTIR spectrometer equipped with a 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 (F) (Sigma-Aldrich) and cyclohexanone (CH) (Sigma-Aldrich) used in catalytic experiments were pre-dried with a molecular sieve 3A to exclude the effect of moisture originating from the chemicals. All catalytic experiments on CH self-condensation and aldol condensation of F and CH were performed by using a 100 ml stirred batch reactor (a glass flask reactor). For these experiments, 0.5 g of freshly calcined catalyst (T= 450 °C) was used (0.5 g of Mg-Al mixed oxide was also used to prepare the reconstructed HTC). 6.5 g of furfural and different amounts of cyclohexanone (6.6-66.4 g, corresponding to CH/F molar ratio in the range of 1-10) were used as a reaction mixture. The experiments were carried out at 25, 50 or 90 °C. In experiments on CH self-condensation 33.2 g of cyclohexanone was used and reaction temperature was in the range of 25-150 °C. After adjusting the desired reaction temperature, a catalyst was added to the reaction mixture, and the reaction was carried out for 180 min at 200 RPM. In experiments with changing stirring rate and catalyst particle size, it was established that the reaction is limited neither by external nor internal mass transfer under the chosen reaction conditions. Samples of liquid products were periodically withdrawn from the reactor during the experiment, diluted with excessive benzene, centrifuged 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  $\mu\text{m}).$  Each catalytic experiment was performed in parallel and the results were used only if the relative error did not exceed 2%.

The composition of reaction products was determined by GC-MS by means of GC-2010 Plus (Shimadzu) unit (MS detector - GC-MS-QP 2010 Ultra; GC column - Rxi-5 Sil MS, Restek, 30 m x 0.25 mm ID x 0.25  $\mu$ m). Catalytic results of aldol condensation of furfural and cyclohexanone were described by conversion and selectivity parameters that were calculated as follows:

reactant conversion(t) (mol%) =  $100 \times (reactant_{t=0} - reactant_t)/reactant_{t=0}$ ;

selectivity to product i = (mole of reactant converted to product i)/(total moles of reactant converted).

Carbon balance was monitored in all experiments as the total number of carbon atoms detected in each organic compound with Cn atoms divided by the initial number of carbon atoms in a feed, similar to the method used elsewhere.<sup>[36]</sup>

The yields of furfuryl alcohol (F-OH) and furoyl furoate (FOOF) determined in reaction products were calculated as the percentage of moles of the corresponding compound per the initial number of moles of furfural in reaction mixture.

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Keywords: furfural • cyclohexanone • aldol condensation • hydrotalcite • mixed oxide

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Mg-Al hydrotalcite-based materials were used as solid basic catalysts for aldol condensation of furfural and cyclohexanone. The activity of reconstructed hydrotalcite with Brønsted basic sites was much higher compared to mixed oxide with Lewis basic sites. Cyclohexanone-to-Furfural molar ratio influenced the composition of reaction products. Catalyst's activity decreased in consecutive catalytic runs due to the formation of heavy reaction products as well as the occurrence of Cannizzaro reaction.