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Influence of Water on the Production of Liquid Fuel Intermediates from Furfural via Aldol Condensation over MgAl Catalyst

Zdeněk Tišler, Pavla Vondrová, Kateřina Peroutková *, Josef Šimek, Lenka Skuhrovcová, Kateřina Strejcová, Eliška Svobodová and Zahra Gholami

Unipetrol Centre of Research and Education (ORLEN UniCRE), a.s, Areál Chempark 2838, Záluží 1,
436 70 Litvínov, Czech Republic
* Correspondence: katerina.peroutkova@orlenunicre.cz

Abstract: The aldol condensation of furfural and acetone is considered a promising method for the production of liquid fuel intermediates. 4-(2-furyl)-3-buten-2-one (FAc) and 1,5-di-2-furanyl-1,4-pentadien-3-one (F2Ac) are the main products of the reaction, which can go through the hydrodeoxygenation process to convert to diesel and jet fuel range fuels. Considering the present situation at the fuel-market related to crude oil shortage, the above-mentioned process seems to be a convenient path to obtain fuels in the diesel and kerosene range. This research focuses on the effect of water on the furfural conversion and product distribution during the aldol condensation. The catalyst chosen for this research was MgAl mixed oxide in molar ratio 3:1. The reaction was performed at 40 °C and 1 MPa in a continuous-flow reactor with and without water in the feedstock. The physicochemical properties of the catalyst were evaluated using different techniques. The catalyst lifetime decreased and the catalyst deactivation started faster by the addition of 5 wt.% water to the feedstock with the furfural to acetone ratio (F:Ac) of 1:2.5. Selectivity to FAc increased by 10% in the presence of water. The catalyst lifetime enhanced by increasing the F:Ac ratio from 1:2.5 to 1:5, in the presence of 5 wt.% water. The furfural conversion was 100% after 28 h of reaction, and then decreased gradually to 40% after 94 h of reaction. At higher F:Ac ratio, the selectivity to FAc was 10% higher, while the F2Ac was about 8% lower.

Keywords: Aldol condensation; furfural; acetone; Mg/Al hydrotalcite; Mg/Al mixed oxide; liquid fuel intermediates

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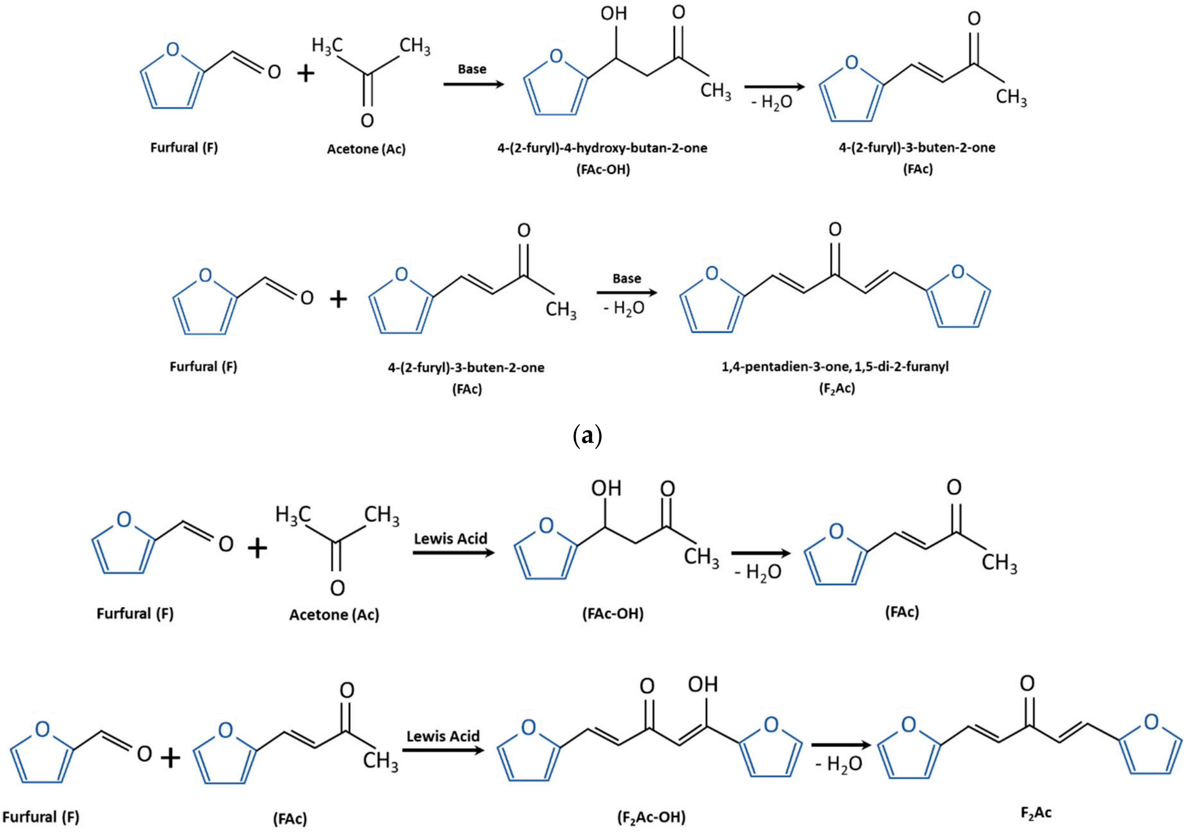
1. Introduction

Due to the depletion of fossil fuel resources, production of biofuels and chemicals from sustainable raw materials is becoming more important for the more efficient and affordable production of fuels and chemicals [1,2]. As an abundant and carbon-neutral energy resource, lignocellulosic biomass is extensively used for the production of value-added chemicals and biofuels via different thermal, biological, and chemical processes [3]. To obtain fuels in diesel and kerosene range (C_8 and C_{13}), it is important to increase the number of carbon atoms in molecules derived from biomass, since the building blocks from biomass usually consists of 3–9 carbon atoms [4]. Furfural, a furanic aldehyde, is a platform molecule produced by dehydration of C5-sugars from hemicellulose and lignocellulosic biomass or is extracted as a residue from acid hydrolysis of sugar-cane, and can be transformed into a wide range of biochemicals and biofuels through different processes such as hydrogenation, nitration, oxidation, decarbonylation, and condensation [5–11]. Aldol condensation is one of the ways to obtain the desired compounds from short-chain aldehydes and ketones, such as furfural, hydrolyzed from biomass, and acetone, as a by-product of phenol synthesis [12]. This reaction aims to prepare molecules with an increased number of carbon atoms from small carbon molecules. Acetone is a by-product from cumene process, which is used for phenol synthesis [13]. The reaction of acetone and furfural over the heterogeneous catalyst results in the formation of C8 molecule of FAc (4-(2-furyl)-3buten-2-one). Moreover, if this product is reacting with another furfural molecule (Scheme 1), the reaction leads to formation of higher carbon compound F_2Ac (1,5-bis-(2-furanyl)-1,4-pentadien-3-one). Other by-products such as mesityl oxide could also be formed through self-condensation of acetone [2,14,15].



(a)

(b)

Scheme 1. Reaction steps of the aldol condensation of furfural with acetone in the presence of (**a**) basic and (**b**) acid sites.

Both acid and basic catalysts can be used for aldol condensation reaction [5], base catalysis usually providing more control, while acids are having more tendency for the oligomerization of furans and products formed in the reaction [16]. Aqueous solutions of hydroxides, such as NaOH or KOH, are homogenous basic catalysts usually used for aldol condensation because of their selectivity [17–19]. However, due to the higher cost and environmental impact of homogenous catalysts on waste waters, it is necessary to develop not only industrially available, but also environmentally acceptable catalysts [12,15]. Heterogeneous catalysts are generally preferred due to the simplicity of their separation from the products and lower corrosion possibility. A comprehensive review on the deployment of solid base catalysts for in organic reactions such as double bond isomerization, hydrogenation, aldol addition, and nitroaldol reaction was performed by Ono and Hideshi Hattori [20,21] and they reported that some metal oxide catalysts (e.g., ZrO_2) have a complex character and in addition to the basic character, they also could act as an acid catalyst for dehydrogenation of alkenes and amines, while some other metal oxides (e.g., MgO) are showing a more simple character [22]. Another catalyst used for aldol condensation are zeolites, which activate carbonyl-containing molecules of the feedstock. Zeolites are Lewis-based catalysts and can promote the course of the aldol condensation [23,24]. Among the solid base catalysts, the layered double hydroxides (LDH) have shown good properties in bio-fuel processes, such as aldol condensation [14,25,26]. LDH's are classified as heterogeneous catalysts with general formula $\left[M^{2+}_{1-m}M^{3+}_{m}\left(OH^{-}\right)_2\right]^{m+}\ \left[\left(A^{x-}\right)_{m/x}\cdot yH_2O\right]^{x-}$, where M^{2+} and M^{3+} indicates divalent and trivalent metal cations, respectively. A^{x-} represents n-valent anion, such as $CO_3{}^{2-}$ $NO_3{}^{-}$, $SO_4{}^{-}$ or OH^{-} [27]. For aldol condensation, a heterogeneous MgAl oxide catalyst is used, which is derived from the above-mentioned hydrotalcite by thermal treatment. These are considered as catalysts with high activity, non-toxicity, high temperature resistance and the cost of these materials is not high [1,28].

The aldol condensation of furfural and different ketones were studied by Huang et al. [16]. The reaction performed in a flow reactor at 100 °C and 0.69 MPa over $MgAl_2O_4$, Al_2O_3, $CaO/MgAl_2O_4$ and $MgO/MgAl_2O_4$ catalysts. The $CaO/MgAl_2O_4$ catalyst showed the highest reaction rate, and it was deactivated after a few hours of reaction mainly due to the formation of 2-furic acid via the Cannizzaro reaction. In another study by Su et al. [3], the aldol condensation of furfural and acetone for the production of liquid fuel intermediates was investigated using Lewis acid zeolite catalysts (Sn-MFI and Sn-Beta). However, both catalysts were active for the reaction, but their activity and selectivity showed a great difference. The products of the reaction over Sn-Beta catalyst (with larger pore size) were a mixture of FAc (40%) and F2Ac (22%), while FAc was the only product of the reaction over Sn-MFI catalyst. Because of the differences in the pore geometry of the catalysts, the Sn-MFI catalyst showed a shape selectivity and resulted in the formation of only FAc. The furfural conversion was also 99% after 2 h of reaction over, while the conversion of 90% obtained over the Sn-MFI catalyst after 9 h of reaction. In addition to the pore structure of the catalyst, the presence of water also can affect the product selectivity, and Su et al. [3] reported that the selectivity to FAc increased by increasing the water content in the feedstock.

In present work, the aldol condensation of furfural with acetone was performed in a continuous-flow reactor over the heterogeneous MgAl catalyst in its rehydrated form. Due to the important role of water in altering the product selectivity, the reaction performance was evaluated in the presence of 5 wt.% of water in the feedstock. The furfural conversion and product distribution were evaluated during the reaction at 40 °C and pressure 1 MPa. Gas chromatography was used to analyze the products of the aldol condensation reaction. The physicochemical properties of the MgAl catalyst were also investigated using different techniques including inductively coupled plasma method (ICP-OES), N_2-physisorption, X-ray diffraction (XRD), thermogravimetric analysis (TGA). Temperature programmed desorption (TPD) analysis was also used for the evaluation of the acid-base properties of the catalyst.

2. Materials and Methods

2.1. Synthesis of Catalyst

The catalyst used for our experiment in present work was used in our previous research [2,5,14,29,30]. MgAl hydrotalcite was prepared with Mg:Al molar ratio 3:1 and was synthesized by co-precipitation method at constant pH value of 9.5, and constant temperature 60 °C. Synthesis consisted of reaction between two aqueous solution with different pH character. Acid solution was prepared from nitrate salts–magnesium nitrate $(MgNO_3)_2.6H_2O$ (Lachner, p.a purity) and aluminum nitrate $Al(NO_3)_3.9H_2O$ (Lachner, p.a purity) and its molar concentration was $c_{Me} = 1\ mol/dm^3$ (Me = Mg + Al). Precipitation was retrieved with basic solution containing of potassium carbonate K_2CO_3 (Lachner, p.a purity) and potassium hydroxide KOH (Lachner, p.a purity), ($c_{KOH} = 2\ mol/dm^3 + c_{K2CO3} = 0.2\ mol/dm^3$). After co-precipitating process, the solution was filtered through high-pressure filtration consisting of paper filters (HOBRA filter, N20) and thoroughly washed with demineralized water until neutral pH was achieved. The separated filter cake was then extruded and dried overnight at 65 °C. Subsequently, the catalyst was in situ calcined and rehydrated (refer to 3.3 catalytic tests).

2.2. Catalyst Characterization

Detailed characterization of structure and surface properties of MgAl catalyst has already been carried out in our previous articles [2,5]. Chemical composition of catalyst was determined by Optical Emission Spectrometer Agilent 725 (ICP-OES, Agilent Technologies Inc., Santa Clara, CA, USA).

X-ray diffraction (D8 Advance Eco, Bruker AXC GmbH, Karlsruhe, Germany) was chosen to characterize the structure of hydrotalcite with 1 kW power X-ray lamp with copper anode CuKα: 1.5418 Å. For the analysis, the sample was milled to powder. The step size of 0.02° and a step time of 0.5 s were used. A range from 5° to 70° 2ndeta for the XRD patterns was retrieved and XRD patterns were then evaluated by Diffrac.Eva software (Bruker AXC GmbH, Karlsruhe, Germany).

Specific surface area (BET) was analyzed by nitrogen physisorption at 77 K using Autosorb iQ (Quantachrome Instruments Boynton Beach, FL, USA). Samples of catalyst were before the analysis outgassed and dried for 16 h at 110 °C in 9 mm glass cell.

The TGA Discovery series (TA Instruments, Lukens Drive, NW, USA) was used to obtain thermogravimetric analysis (TGA), where ~20 mg of sample was weighted in an open aluminum crucible operating at 10 °C/min ramp temperature in a range of 40 to 900 °C under nitrogen (20 mL/min, Linde 5.0). To determine sample fragments, the Quadrupole mass detector OmniStar GSD320 (Pfeiffer Vacuum Austria GmbH, Vienna, Austria) was used.

TPD-CO_2 and TPD-NH_3 was used to determine acid-base properties using Autochem 2950 HP (Micromeritics Instrument Corporation, Norcross, GA, USA). Prior to the analysis, ~100 mg of sample was measured into quartz U-tube reactor. In both analysis, sample was pre-treated in He at 500 °C with heating rate 10 °C/min. In TPD-CO_2 analysis, to determine basic active sites, sample was cooled down to 50 °C and then saturated with CO_2 gas (10 wt.% CO_2 in He, 25 mL/min). Subsequently, the gas was changed to He (25 mL/min) in order to remove weakly adsorbed carbon dioxide molecules until the baseline was stabilized. Then, the sample was heated up to 900 °C (15 °C/min) and TPD curve was obtained using TCD detector. Temperature programmed desorption of ammonia (TPD-NH_3) was carried out using the same conditions to determine acid active sites of the catalyst, except the gas was changed to NH_3 (10 wt.% NH_3 in He).

2.3. Catalytic Tests

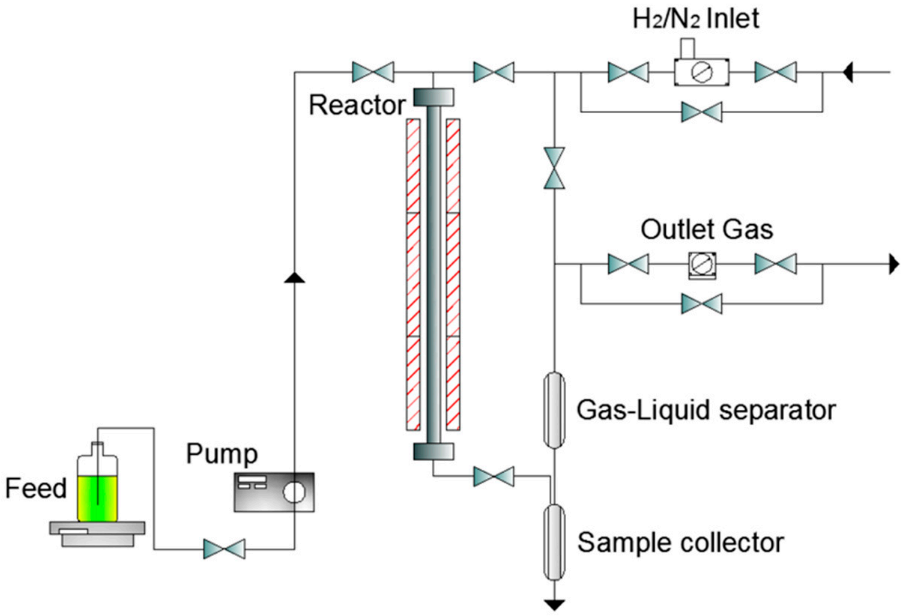
Influence of adding water to the feedstock furfural (Sigma Aldrich, p.a. purity) and acetone (>99%, Penta s.r.o, Prague, Czech Republic) was the main point of our research; therefore, we decided to study two molar ratios of feedstock F:Ac 1:2.5 and 1:5 with addition of 5 wt.% of water. Tests were also performed without water in the reaction mixture for comparison and over regenerated catalyst. Table 1 shows an overview of the tests performed. Reproducible amount of experiments were carried out in a batch reactor used in our previous research [30], but at present study a continuous-flow stainless steel reactor (AISI 316L) was used at an experimental unit, located in UniCRE (ORLEN UniCRE) in Litvínov, Czech Republic. The length of the reactor was 700 mm with an inner diameter of 17 mm and was equipped with 5 mm wide thermos tube and three thermocouples (430, 359, 288 mm) located at the beginning, center and at the end of catalytic bed. For secondary product collection and evaporation, the reactor was equipped with water cooling in the reactor outlet.

Prior to each experiment (Table 1, test 1–2a, 3), 5 g of MgAl catalyst was loaded into the reactor and activated by calcination; firstly the temperature was raised to 250 °C (ramp 100 °C/h) and kept for 1 h, then raised to 350 °C (also kept 1 h) and then raised to the final temperature of 450 °C, which was kept for 4 h in the flow of inert gas (N_2, 5 L/h). After activation of the catalyst, temperature was lowered to 40 °C (by nitrogen flow) and the pressure was set to 1 MP and the catalyst was rehydrated with distilled water for 8 h (flow 10 g/h). After this procedure, the feedstock of F:Ac started to flow into the reactor (10 g/h). For the reactions in the presence of water, 5 wt.% of water was also added to the mixture of

F:Ac, then the mixture with the total flow of 10 g/h was pumped into the reactor. After the last sample was taken, the catalyst was regenerated (test 2b): flow of feedstock (F:Ac) was stopped together with the pressure and acetone was then pumped into the reactor (80 g/h) for the next 10 h. Subsequently, the flow of nitrogen was increased to a maximum for 6 h. After flushing the catalyst with nitrogen, the catalyst was rehydrated with water and then activated using the same conditions as above-mentioned fresh catalyst. The simplified diagram of the reactor set up is shown in Scheme 2.

Table 1. The reactions overview of F:Ac experiment in flow-through experiment.

Test No.	Catalyst	Molar Ratio	Water Addition	Feed Flow [g/h]
1.	MgAl 3:1	1:2.5	-	10
2a.	MgAl 3:1	1:2.5	5 wt.%	10
2b.	MgAl REG	1:2.5	5 wt.%	10
3.	MgAl 3:1	1:5	5 wt.%	10



Scheme 2. The reactor set up of the aldol condensation of furfural with acetone.

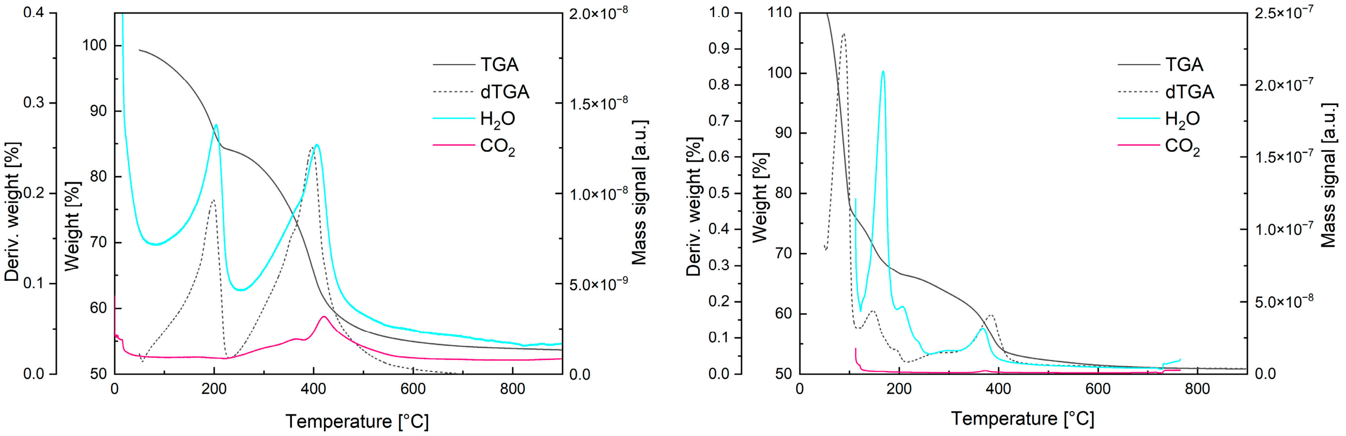
To analyze the product mixture, samples were taken every two hours for analysis by gas chromatograph Agilent 7890 (Agilent Technologies Inc., Santa Clara, CA, USA) equipped with a flame ionization detector (FID) using HP-5 capillary column (30 m/0.32 mm ID/0.25 µm).

3. Results

3.1. Catalyst Characterization

Textural analysis of MgAl catalysts used in this work, was already thoroughly carried out in our previous research [2,5,30]. Thus, to preserve integrity, essential characteristics were used in present study. A layered-double hydroxide precursor MgAl 3:1 (LDH) made by co-precipitation process, was tested to determine elemental composition using the inductively coupled plasma method (ICP-OES). Compared to the desired theoretical molar ratio 3:1, the molar ratio 3.45:1 (25.0 wt.% of Mg, 8.0 wt.% of Al) was determined, which may have been due to the use of nitrate salts during the synthesis of the catalyst, as the number of water molecules in nitrate salts may be slightly different than declared. This catalyst was chosen according to our previous research [1], where the study showed that the molar ratio 3:1 achieved the highest conversion of furfural.

Thermogravimetric analysis (TGA) together with derivate thermogravimetric analysis (dTGA) were carried out to determine changes in dried MgAl (MgAl, Figure 1a) and rehydrated MgAl (MgAl REH, Figure 1b). A graphical presentation of both TGA and dTGA analysis for the two tested samples can be seen in Figure 1a,b, where several decreases in the MgAl mass weight are visible as the sample was thermally decomposed. In the low-temperature phase of analysis, the decrease in catalyst mass due to water removal from the surface and inner layers of the sample was observed, which also corresponded with the high temperature peak at 200 °C during dTGA analysis (Figure 1a). The second phase of weight reduction occurred around 45 wt.% at the higher temperature of 280–400 °C for TGA and in the 400 °C area for dTGA analysis, which was due to the removal of carbonate anions and hydroxyl groups from the double-layered hydroxide structure. As for the MgAl REH (Figure 1b), there was an obvious decrease in the mass weight (up to 37 wt.%) at 100 °C, which corresponded to the intense peak in this temperature area in the dTGA analysis. This was due to the removal of residual water in rehydrated catalyst. At 400 °C evaporation of carbonate anions and hydroxyl groups was observed. However, the intensity of the peak was lower than at MgAl. Release of water and carbon dioxide was observed using mass spectroscopy, which corresponded to the exact temperature of molecule release during the analysis, as described above. For the MgAl sample, the release of CO_2 was significantly higher than in rehydrated catalyst, where CO_2 was absorbed during the analysis and only a little peak was observed from the mass signal.



(**a**) (**b**)

Figure 1. TGA and DTG analysis, with H_2O and CO_2 mass spectrometry, (**a**) MgAl, (**b**) MgAl REH.

X-ray diffraction method (XRD) was used to determine crystallinity of tested samples including MgAl (only dried), MgAl REH, and calcined MgAl (MgAl CALC) used in present work (Figure 2). For the dried MgAl, a typical pure phase reflection of hydrotalcite was obtained according to sharp diffraction lines at 11.4°, 22.9°, 35.0° and 61.0°, corresponding to planes, (0 0 3), (0 0 6), (0 0 9) and (1 1 0) (JCPDS 70-2151). Similar results also showed XRD for MgAl REH sample, where rebuilding of the layered structure took place and material was transferred to maixnerite ($Mg_6Al_2(OH)_{18}{\cdot}4H_2O$). A sharp diffraction line indicated well-crystalized phases with defined crystals corresponding to the MgAl results. However, for the MgAl CALC sample, two broad peaks with low intensity were observed in the XRD pattern, which characterized diffraction line at 43.2° and 63.0° reflections (JCPDS 77-2179). The decrease in crystallinity was caused by calcination under nitrogen atmosphere at 450 °C, which led to the destruction of layered structure, typical for LDH, and to the distribution of homogenous Al_2O_3 in MgO lattice [1].

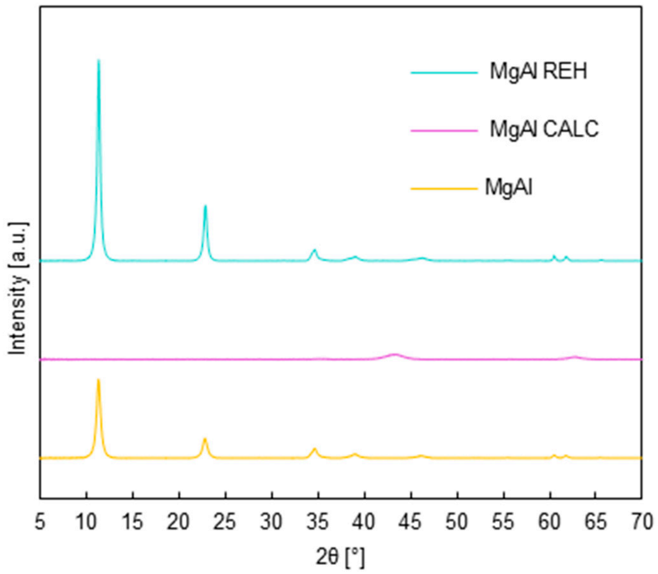


Figure 2. XRD patterns for tested catalysts.

Specific surface area (BET) of the sample before and after calcination and of the rehydrated catalyst, was obtained using nitrogen physisorption at −196 °C (Table 2). For the MgAl sample, the surface area and total pore volume were 73 m^2/g and 0.308 cm^3/g, respectively. Surface area of MgAl CALC was considerably higher than at the uncalcined sample, 242 m^2/g with the total pore volume 0.767 cm^3/g. This result was due to calcination, which led to change into well-dispersed oxide and thus, to the destruction of LDH structure, which was explained in the above-mentioned TGA-MS and XRD results. Moreover, the incorporation of Al^{3+} into Mg^{2+} lattice in the structure of the catalyst occurred, which corresponded to an increase in pore volume in calcined sample [28,31]. Subsequent rehydration of sample (MgAl REH) resulted in the decrease in surface area to 61 m^2/g, together with decrease in pore volume to 0.260 cm^3/g. The decrease in surface area and pore volume was due to reverse reconstruction of double layered structure (LDH), which led to cluster formation and subsequent closure of mesopores [9,32]. In neither tested sample was the presence of micropores observed.

Table 2. Textural and acid-based properties of tested catalysts for aldol condensation.

Sample	Surface Area (BET) [m^2/g]	Pore Volume [cm^3/g]	Total Concentration of Active Sites [μmol/g]	
			Acid-NH_3	Basic-CO_2
MgAl	73	0.385	-	-
MgAl CALC	242	0.654	751	1192
MgAl REH	61	0.260	-	-

The strength and number of active basic and acid active centers were determined using the temperature programmed analysis, TPD-CO_2 and TPD-NH_3, respectively. Analysis of MgAl CALC used in present study in terms of acid-base properties was already thoroughly described in our previous articles [2,29]. The TPD-CO_2 showed an asymmetric peak at 100–130 °C area corresponding to weak basic site (weak Brønsted OH groups). The peak in the 150–180 °C area indicated a medium strength basic site containing metal-oxygen pairs and in the 200–250 °C area a strong basic site. Temperature programmed desorption of ammonia of acid centers showed two peaks. The first peak at 115 °C corresponded to a weak acid site and at the second one at 188 °C suggested subsequent desorption of stronger bounded NH_3 molecules from Lewis acid sites. Generally, aldol condensation can be catalyzed by all basic sites in the surface including Lewis O^{2-}, Me^{n+}-O^{2-} pairs and Brønsted OH^{-} sites. As it was reported, Me^{n+}-O^{2-} pairs is the dominant active site for this reaction. These results are in agreement with other previous studies [2,13,32]. The total consumption of both gases for the annealed MgAl CALC sample is indicated in Table 2.

3.2. Influence of Water Addition and Molar Ratio into F:Ac Feedstock on Selectivity

The progress of aldol condensation of furfural with acetone with different molar ratio of furfural to acetone (F:Ac) by addition of 5 wt.% water was investigated in a continuous-flow reactor at constant temperature of 40 °C, constant pressure of 1 MPa and feed flow of 10 g/h over MgAl catalyst in molar ratio 3:1. Gas chromatography (GC) analysis was performed during the experiment and showed the presence of the desired products along with additional products. It took about 6 h for the reaction to be stabilized and the products started to be analyzed from 8 h of reaction start up. The reactions continued until deactivation of the catalyst occurred.

The results are shown graphically in Figure 3a,b and overview of experiments in Table 1, where a comparison of the reaction of furfural with acetone (I) without water (test 1), (II) with water (test 2a) at a molar ratio of F:Ac, 1:2.5, can be seen. The conversion of furfural for test without water (Figure 3a) was maintained at 90% up to 26 h of reaction, whereas for the reaction with the addition of water to the feedstock, there was a slight, and later a significant, decrease from 12 h of the test and from 22 h onwards (Figure 3b). This steep decrease was observed for the test without water addition only after 34 h of the test. However, in contrast, when water was added to the feedstock, an increase in selectivity for the major product FAc (4-(2-furyl)-3-buten-2-one) from 71% to 80% was observed compared to the test without water. The selectivity to FAc was constant over the duration of the test until 26 h, where the catalyst slowly started to show an initial deactivation. Additionally, a gradual decrease was observed from the beginning of the test with the addition of water to the feedstock.

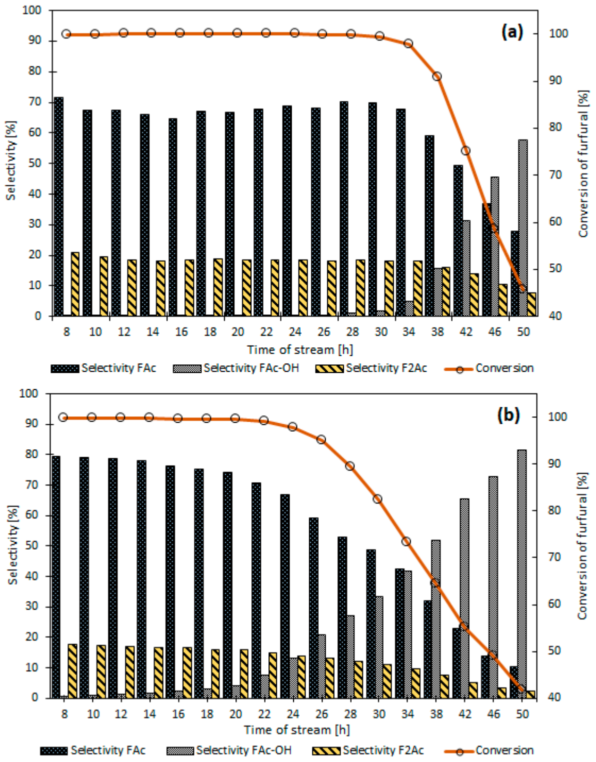


Figure 3. Aldol condensation of (**a**) furfural with acetone in molar ratio 1:2.5, (**b**) furfural with acetone in molar ratio 1:2.5 with 5 wt.% water addition. Tests were performed in a continuous-flow reactor at constant temperature 40 °C and pressure 1 MPa, flow of feedstock 10 g/h.

The subsequent reaction of the FAc product with another molecule of furfural resulted in the formation of F2Ac (C_{13}), which can also be seen in Figure 3a,b, where the F2Ac product showed (as with FAc) a decrease from the beginning of the experiment. The selectivity of the F2Ac was initially about 5% lower in the reaction with the water in feedstock than the reaction without water. The presence of strongly basic sites in the catalyst is necessary for the formation of this product [5]. This was already discussed in the text above (refer to 3.1. Catalyst characterization) and also discussed in study of Čapek et al. [33,34], where authors determined that catalytic activity could be influenced by the increasing distribution of basic sites and presence of medium and strong basic sites, which are typical for MgAl catalyst. The decrease in selectivity for both desired products, i.e., FAc and F2Ac, showed that the addition of water to the feedstock very negatively affects the amount of these basic sites. This issue has already been addressed in the previous studies [5,30], where the effect of the water addition on the aldol condensation process of furfural with acetone was tested, but only in a laboratory batch setup. The water molecules together with furfural and acetone competed for the same active sites in the catalyst, which prevents the active feedstock from binding into the catalyst lattice. At the same time, the presence of water shifted the equilibrium of the dehydration steps, thereby limiting the possibility of converting intermediates to the final product. This can also be seen in Figure 3b, where an increase in the intermediate FAc-OH was observed; an intermediate that is also marked in Scheme 1. On the other hand, in the study of Parejass et al. [26], it was discovered that the higher content of the water in the feedstock, the better the conversion of furfural. However, this outcome negatively affects the selectivity of the desired product F2Ac by decreasing it [26,35]. This is due to the fact that water weakens the double bond of furfural (C=O), causing an increase in reactivity in the presence of water. Another factor that may have influenced the F2Ac production was the reaction temperature of 40 °C. This has already been confirmed in the study by Hora et al. [1], who mentioned that increasing the reaction temperature improves the dehydration of FAc, leading to a higher selectivity to the F2Ac (C_{13}) product. In addition to basic sites, the mixed oxides contain acidic sites, which are required for dehydration of the condensation products FAc-OH and F2Ac-OH (Scheme 1). As shown by the obtained data, the addition of water to the feedstock caused a rapid increase in FAc-OH in the reaction product (Figure 3b), whereas when water was not added, FAc-OH started to appear only at the onset of catalyst deactivation, i.e., around 26 h of the test (Figure 3a). Xu et al. [36] used the magnesium hydroxide fluorides MgF_2 x(OH)x as catalyst for aldol condensation of furfural and acetone (F:Ac = 2) at 50 °C in a batch reactor. They observed that the main product was furanic dimer F2Ac with about 70%. However, the furfural conversion at the given reaction condition was between 13–34%. The reaction mechanism of furfural aldol condensation over MgAl catalyst was performed by Tampiery et al. [37] it was found that the adsorption has a significant effect on the product distribution as well as the catalyst deactivation. FAc-OH and FAc with high selectivities were observed at the beginning of the reaction, while by prolonging the reaction FAc-OH was dehydrated and transformed to F2Ac. It was also reported that a high concentration of FAc-OH enhance the deactivation rate, which is in good agreement with finding of the present study, where the furfural conversion decreased by increasing the reaction time and formation of more FAc-OH. Afterwards, a test with regenerated mixed oxide, MgAl (test 2b) was performed. In Figure 4a, it can be seen that the trend of the reaction was very similar to that of the fresh catalyst, but the catalyst deactivation occurred much earlier, after 16 h of the reaction. However, compared to the no-water test (Figure 3a), there was an increase in selectivity FAc in the case of regeneration (Figure 4a). This was due to the activation of Brønsted base centers and OH^- groups on the catalyst surface, which lead to an increase in catalyst activity [10,38]. These results corresponded with the above-mentioned discussion and catalyst characterization, where regeneration leads to irreversible changes in the textural properties of the catalyst (analyzed via XRD). Moreover, these changes were influenced not only by the textural properties, but also by the state and structure of active sites, which in contrast to test 2a, was the reason for the much faster catalyst deactivation. Additionally, the regeneration of the catalyst could have been influenced by test 2a, which was carried out almost to the end of the reaction (deactivation of the catalyst). Carbon deposits formed by high molecular weight condensation products could have caused irreversible damage to the catalyst during annealing. Under industrial conditions, regeneration of the catalyst would be carried out early in the deactivation process, which would certainly contribute to the stability of the catalyst [39]. In the case of aqueous media, the Cannizzaro reaction occurs, producing furoic acid, which has been previously demonstrated [6]. Interaction of the furoic acid with the base centers of the catalyst occurred, leading to a decrease in catalytic activity.

Another test for aldol condensation of furfural with acetone (test 3) was carried out in a molar ratio of 1:5 (F:Ac) again with 5 wt.% of water in the feedstock under the same conditions mentioned above. The comparison showed that increasing the molar ratio of F:Ac from 2.5 (Figure 3b) to 5 (Figure 4b) had a significant positive effect on the stability of the catalyst, resulting in an increase in the time to 100% furfural conversion, which increased from 20 h to 28 h, approaching that observed in the test without the addition of water (test 1). Along with this increase in time, an increase in selectivity to FAc product was also observed, from 80% to more than 90% (an increase of more than 20% compared to test 1 for the reaction without water). The increase in the molar ratio of F:Ac has also led to a decrease in selectivity to F2Ac (selectivity to F2Ac was only about 10%), which was due to the fact that there was no longer enough furfural available in the feedstock for the next condensation step. The process of catalyst deactivation is generally much more gradual than in the case of the F:Ac test, 1:2.5, which showed a fast deactivation after 34 h of reaction and reached 45% after 50 h of reaction.

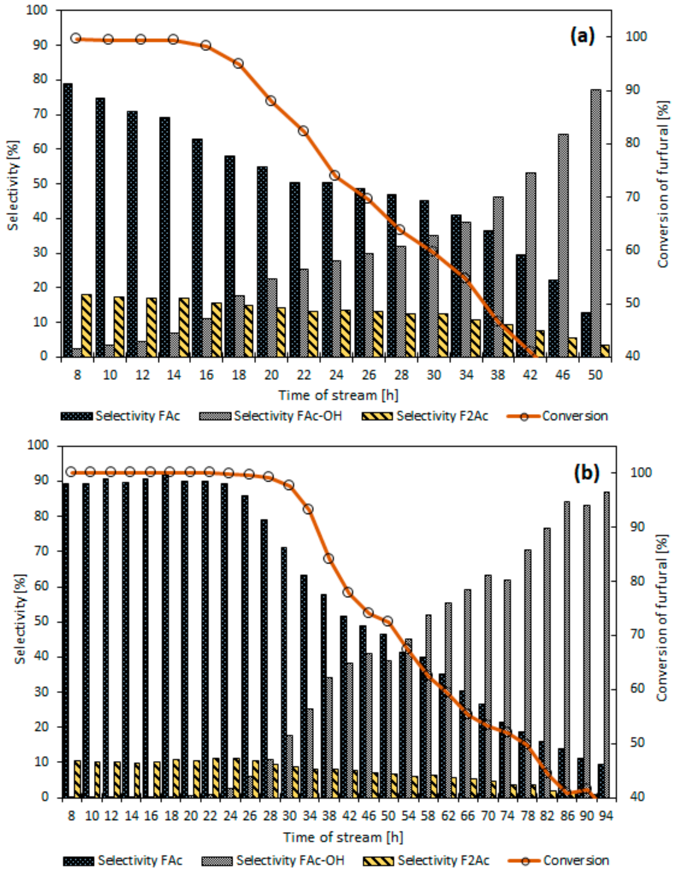


Figure 4. (**a**) Aldol condensation of furfural with acetone in molar ratio of 1:2.5 with 5 wt.% water over regenerated MgAl catalyst, (**b**) furfural with acetone in molar ratio 1:5 with 5 wt.% water addition. Tests were performed in a continuous-flow reactor at constant temperature 40 °C and pressure 1 MPa, flow of feedstock 10 g/h.

3.3. Metal Content in Feedstock during the Aldol Condensation of Furfural with Acetone

During the aldol condensation of all tests in the present work with F:Ac at a ratio of 1:2.5, the metal content of Mg, Al, and Fe in the products during the reaction was analyzed. The metal abundance is graphically described in Figure 5. The metal content increased with the catalyst deactivation in all tests, i.e., during the formation of acidic products, mainly FAc-OH. The largest increase in Al was observed in the presence of water in the feedstock (Figure 5b). The iron from the reactor walls could leach into the product mixture due to the corrosion caused during the reaction. The iron content increased during the reaction without water (Figure 5a) as the catalyst was initially deactivated. For the reaction with water (Figure 5b), Fe appeared at a higher concentration (0.8 ppm) in the early stages of the reaction, indicating that water had high corrosive effects on the reactor walls with the F:Ac feedstock. However, a steady state then occurred during the test and as can be seen, it was not present in the product mixture towards the end of the test. In the case of the regenerated MgAl catalyst (Figure 5c), the iron leakage into the feedstock was significant, which was due to the disruption of the reactor walls during annealing and rehydration process during in situ regeneration. As for the Mg abundance in the raw material, the largest increase can be observed in the case of the water test, where together with Al considerably increased in the last part of the experiment. This increase was associated with a decrease in furfural conversion (Figure 3b), which was observed in the 28-h test. In the case of the test without water and with a regenerated catalyst, both metals were released in small amounts of Mg and Al due to the effect of the feedstock on the MgAl catalyst.

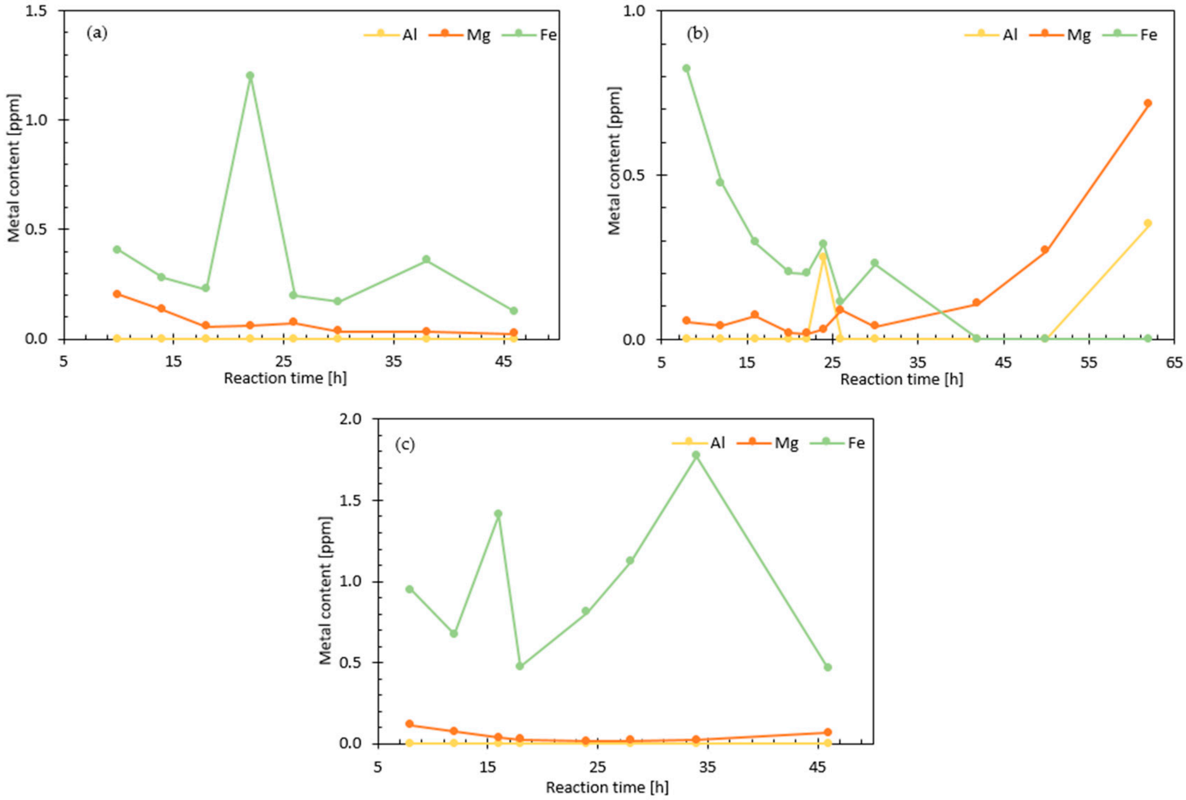


Figure 5. Metal content in products from aldol cond., (**a**) 1:2.5 (F:Ac); (**b**) 1:2.5 with 5 wt.% H_2O; (**c**) 1:2.5 with 5 wt.% H_2O over regenerated catalyst. Tests were performed in a continuous-flow reactor at constant temperature 40 °C and pressure 1 MPa, flow of feedstock 10 g/h.

The addition of water to the F:Ac feedstock in a molar ratio of 1:2.5 significantly affected some of the reaction parameters. As for the negative effect, the earlier deactivation of catalyst during the reaction was observed, in contrast to the reaction without water. However, there was a favorable increase (10%) in the selectivity of the desired FAc product.

At the same time, the addition of water was found to significantly increase the formation of the FAc-OH intermediate, which was already observed early in the reaction. For the second desired product with a higher number of carbons, F2Ac, the selectivity was reduced when water was added to the feedstock. The reaction with regenerated catalyst showed that water positively affected the selectivity of FAc as well as F2Ac. However, there was a significant reduction at the time of 100% furfural conversion in the reaction using regenerated catalyst (already at 16 h of experiment), compared to the reaction without water using the MgAl catalyst. The catalyst lifetime increased at higher F:Ac ratio, and the conversion remained constant at 100% for about 28 h and then gradually decreased to 40% after 94 h of reaction. The FAc selectivity was about 10% higher than the reaction at lower F:Ac ratio, while the F2Ac was about 8% lower. At the same time, the corrosive environment of the continuous-flow reactor could have an influence on the final progress of the reaction with water, since there was an increase in the iron content in the feedstock at the post-reaction start. The overall progress of the aldol condensation of furfural with acetone in the presence of MgAl mixed oxide catalyst possessing active basic centers could have also been affected depending on the acidity of the furfural used in the feedstock. This was also shown in the study of Kikhtyanin et al. [40], where they found that the acidity of furfural is influenced not only by its origin but also by storage and processing. They tested furfural from several distributors using aldol condensation and found that the greater the acidity of furfural, the earlier the deactivation of the catalyst. However, if the furfural is pre-distilled, the resulting activity of the rehydrated catalyst improves and hence the resulting furfural conversion.

As shown by the reactions with MgAl catalysts based on hydrotalcite materials, these materials can be effectively used and are equivalent to a number of other catalysts previously tested in this type of reactions (zeolites, MOFs, functionalized organic resins or quartz materials, etc.). Only zeolite catalysts could provide better resistance to deactivation in the presence of water. In the case of other materials, as in the current study, the deactivation of catalysts caused mostly by hydrolysis of silica or leaching of the active site due to hydrolysis was observed [23,41,42]. For possible subsequent industrial applications, the shape of the catalyst will also play a significant role and new modern methods such as 3D printing can significantly contribute to improving the properties of catalysts for these reactions as well [8].

4. Conclusions

This study focused on the aldol condensation of furfural with acetone over MgAl catalyst with the molar ratio of 3:1 prepared by co-precipitation method. Catalyst activity was evaluated in a continuous-flow reactor at 40 °C and 1 MPa. The effect of 5 wt.% water in the feedstock on the catalytic performance and product selectivity of the reaction with furfural to acetone ratio of 1:1.5 confirmed that the water can significantly affect the catalyst stability and lifetime. The furfural conversion of 100% was observed for both conditions, while catalyst deactivation started 12 h earlier in the presence of water. In spite of its negative effect on the catalyst activity and furfural conversion, the selectivity to FAc increased by 10% in the presence of water. Nevertheless, this increase was found out to be negative for dehydrating properties of MgAl catalysts, because of simultaneous increase of by-product FAc-OH, which is an intermediate during the aldol condensation of furfural. It was observed that selectivity of this intermediate increased with water addition during the aldol condensation and reduced basic properties of catalysts. This also resulted in faster deactivation of the catalyst in comparison to tests without water. Results also showed that an increase in the molar ratio of F:Ac (from 1:2.5 to 1:5) with water addition has a positive impact on prolonging the catalyst lifetime and compared to reaction without water and lower F:Ac ratio. The FAc production increased by over 20% at higher F:Ac ratio. The aldol condensation reaction over the regenerated catalyst resulted in a faster decrease of furfural conversion due to the changes in structure and decrease in the number of basic sites, thus the catalyst lifetime was shorter. Additionally, metal content was measured during the reaction, where results showed an increase in Fe, which was released from reactor walls, during the first hours of experiment because of the water addition. In the future industrial use of F:Ac feedstock in aldol condensation, it will be necessary to watch not only the feedstock purity, but also with water addition will be also possible to manage final composition of condense products.

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