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CATALYST-ASSISTED CONVERSION OF PYROLYSIS BIO-OIL INTO FUELS

Abstract

The aldol condensation of model compounds furfural and acetone on the selected base catalysts have been performed. The activity of MgO was compared with industrially produced hydrotalcite and the series laboratory prepared hydrotalcites.

$Si\times MAl_2O_4$ hydrotalcites (M = Mg, Zn, Ni, Co, Cu, and Fe) were prepared by the sol-gel method at low calcination temperature of 300°C. The properties of the catalysts were evaluated by XRD and BET technique and they had a mesoporous structure. The aldol condensation was performed in the liquid phase preferably in N_2 atmosphere, the temperature range of 25-140°C and at elevated pressure. The main condensation products were C_8 FAc monomer and C_{13} F_2Ac dimer. The first intermediate FAc_{ol} was readily dehydrated and higher temperatures favoured the reaction. The furfural (F) conversion into the C_8 product (FAc) from 55.9 up to 94.5% with the selectivity 41.0- 79.5% was reached.

In the comparative tests of MHT hydrotalcites performed at 140° C, the best results were obtained in the case of Zn and Mg hydrotalcites despite their low specific surface. High selectivity to F_2Ac was observed with Ni and Co hydrotalcites as catalysts with the specific surface area of 178 and 246 m^2/g, respectively. As the key parameter for the high conversions the ratio catalyst/furfural close to 0.3 was notified.

Keywords: *aldol condensation; hydrodeoxygenation; hydrotalcite; furfural; acetone; MgO.*

Abbreviations:
AC - aldol condensation
FAc - C_8 product: 4(2-furanyl)-3-buten-2-one
F_2Ac - C_{13} product: 1,5di(2-furanyl) 1,4-pentadiene-3-one (F_2Ac)
FAcol - C_8 product: 4(2-furanyl)-4-hydroxy-2-butanone

1. Introduction

The bio-oil production by the flash pyrolysis of lignocellulosic waste is possible way to generate alternative fuels and specific chemicals. The crude bio-oil need elimination of hydroxyl and carboxylic acid content and conversion of oxygen molecules to hydrocarbons. One way for the fuel production from crude bio-oil is its separation into a hydrophilic and hydrophobic fraction extraction with water. In the hydrophilic fraction of bio-oil, a low molecular weight substances are present (a variety of aldehydes, ketones, organic acids and alcohols). These can be converted to compounds with a higher molar mass by an aldol condensation reaction.

The aldol condensation, as a catalytic route for the formation of C-C bonds between the carbon chains, comprises the condensation of two compounds with carbonyl groups to form higher alcohols and ketones. Oxygen compounds with a boiling point in the distillation range 100°C - 150°C can be further converted into hydrocarbons by catalytic hydrodeoxygenation process. In the case of C_2-C_3 carbonyl compounds (e.g. furfural, acetone) C_8-C_{15} n-alkanes are obtained. It is an essential reaction for upgrading of bio-oils derived from biomass. For an aldol condensation of aldehydes and ketones either basic or acidic catalyst are used [1-5]. The aldol condensation of various furfurals (furfural, methyl furfural, and 5-hydroxylmethyl furfural (HMF)) and ketones (acetone, acetol, dihydroxyacetone, 2-hexanone, etc.), is used as a model reaction for the selection of suitable catalysts for upgrading of the hydrophilic share of bio-oil. The research was focused on the preparation and modification of the catalyst, on the procedure for their activation. Also, it was focused on the variation of the reaction conditions (temperature, pressure, reaction time, catalyst type) in order to obtain the maximum conversion of the starting materials as well the selectivity of the targeted products as FAc, F_2Ac.

Hora *et al.* [2] reported the condensation of furfural and acetone catalyzed by Mg-Al hydrotalcites and Mg-Al mixed oxides with the Mg/Al ratio 2 - 4. The various reaction temperatures (20-100°C) were tested as well as some methods of catalyst activation (calcination and rehydration). The products C_8 to C_{13} were obtained. The reaction temperature as high as 100°C accelerated dehydration and formation of the reaction products. The highest yields were obtained with the calcined catalyst Mg/Al = 3. At 100°C, the conversion of furfural to C_8 and C_{13} higher than 95% with 90% selectivity was reached. When the catalyst was hydrated in situ its activity increases.

In addition to Mg-Al mixed oxide and Mg-Zr mixed oxide, MgO appears as a convenient and inexpensive catalyst. However, it has a low surface area. It can be activated by the heat from $MgCO_3$ as the precursor to the mesoporous material with a high specific surface area. Barthey *et al.* [6] synthesized MgO catalyst with high surface area, 250-300 m^2/g by thermal decomposition of different precursors such as $Mg(OH)_2$, $MgCO_3$, $(MgCO_3)_4 \cdot Mg(OH)_2$ and MgC_2O_4. The optimum calcination temperature was 450°C with the calcination temperature range of 350-800°C. By increasing the temperature, the surface area significantly decreases.

The use of a combination of the calcination processes, hydration and subsequent repeated calcination is described in order to transform the non-porous structure of natural dolomite into the catalyst with higher surface area and smaller crystal size [3]. The density (number) of strong basic centers on the catalyst has significantly increased after the hydro-dehydrating process. The effectiveness of this procedure was tested for the aldol condensation, at temperatures 20-100°C and was compared with the efficiency of NaOH as a catalyst. Activated dolomite was a promising catalyst to produce C_{13} dimers that can be transformed by hydrogenation and deep hydrodeoxygenation in high-quality diesel fuels.

The zeolites of different structures were used as catalysts for aldol condensation of furfural and acetone in the batch reactor at temperatures 20 to 100°C and the reaction time of 0-24 hours. In the presence of a solid acid catalyst, the formation FAc is reached, which is the main product of the primary aldol condensation also in the presence of basic catalysts. However, the following transformation of FAc to $(FAc)_2$ takes place via dimerization of the olefinic FAc on the acid sites [1]. During the reaction, the activity of the investigated zeolite was reduced with the formation of carbon deposits inside the micropores. Calcination can fully restore the catalytic properties of zeolites in aldol condensation of acetone and furfural at temperatures of 500°C [1]. The high conversion of furfural up to 99.6% was also achieved with the MgO/NaY catalyst load of 20% at temperature 85°C [7].

The aldol condensation leads to deactivation of the catalyst by the surface changes. In order to minimize the deactivation of the catalyst, a modification of catalysts ($MgO\text{-}ZrO_2$ and $MgO\text{-}Al_2O_3$) with the addition of Pd (2%) was tested. The aldol condensation was carried out at a pressure of 1013 kPa and a temperature of 50°C, in N_2 or H_2 atmosphere [8]. This modification gently changed the morphology and surface chemistry of the catalysts. The presence of palladium and a reducing atmosphere, lead to a partial hydrogenation of the condensation and preventing the permanent deposition of heavier condensed products on the catalyst surface. For the untreated catalysts (mixed $MgO\text{-}Al_2O_3$ oxides) the activity decreased up to 90% [8].

In recent years, an important position between the basic nanostructured catalysts has gained the oxides with the spinel structure. Especially aluminates of MAl_2O_4 type were characterized by high thermal stability, mechanical robustness and low surface acidity. The spinels have a high resistance to acids and alkalis, which would be desirable for the aldol condensation directly in the bio-oil. Spinels $CoAl_2O_4$, $ZnAl_2O_4$, $MgAl_2O_4$, prepared by carbon route synthesis, were tested for the aldol condensation of HMF (hydroxymethylfurfural) and acetone. For the reaction conditions: temperature 140°C, the HMF/catalyst ratio of - 2 [g/g] after 7 hours, a 100% conversion of HMF was reached. The selectivity for FAc and F_2Ac products was 71-81% and 9-11%, respectively. Comparable results were obtained with the binary spinels, e.g. Ru/Co Al_2O_4 and $Cu/MgAl_2O_4$. The best results were obtained for catalysts containing magnesium [10].

The nanohybrid catalysts (alkaline oxide nanoparticles fused with single or multiwall carbon nanotubes) were also tested in the aldol condensation and subsequent hydrogenation of furfural and acetone isolated from biomass. The water-oil suspension was created by using decalin; the aldol condensation ran at temperatures of 80-100°C and the subsequent step was hydrogenation carried out at 100°C for 1-3 h [11]. The aldol-condensation reaction of furfural and acetone was more effective in an emulsion system than in single aqueous phase. By incorporating active metals (Pd or Pt) onto the nanohybrids, it is possible to hydrogenate the aldol condensation products in the same emulsion system to more stable intermediate products [11].

Khytianin *et al.* [12] studied aldol condensation of furfural with acetone in a continuous tubular fixed bed reactor at 50°C using calcined hydrotalcite with Mg/Al ratio of 3 as a catalyst. Complete conversion of furfural and stable catalyst performance was obtained during the initial 50 h of the test. This period was followed by a rapid catalyst deactivation by the higher molecular weight products (bulkier compounds than F_3Ac_2 and F_2Ac_3) that are less prone to desorption than Brønsted basic sites of catalyst, thus restricting/preventing the access of reactants to active sites. Further investigations of formation of the heavier compounds and particularly of their interaction with the catalyst surface are needed [12].

The aim of this research was to test the suitability of selected solid base catalysts for aldol condensation of the hydrophilic portion of bio-oil. A model reaction of aldol condensation of furfural and acetone was chosen for this purpose. The results of the reaction with more common types of catalysts, i.e., hydrotalcite or MgO carried out with the aim of identification of the optimum conditions are referred. Six prepared catalysts based on hydrotalcites and industrially produced hydrotalcite were tested for their selectivity for the formation of C_8 and C_{13} products. The results obtained are compared with data available in the literature.

2. Experimental

2.1 Preparation and activation of catalysts

For the aldol condensation, heterogeneous basic catalysts were used: commercially available hydrotalcite Hybot MA (ASTIN Catalysts and Chemicals Ltd., Litvínov) activated at 450ºC for 4 hours, the ratio of Mg/Al was 2.2, pore diameter 53.3 nm. MgO catalyst with high specific surface area was obtained from the precursor base $4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$ by annealing at 450°C for 4 hours [6]. MgO sample was mesoporous with pore diameter 46.6 nm and specific area 170 m^2/g.The brown mud from Al_2O_3 production (Slovalco Žiar n. Hronom, Slovakia) with content of 30-35% Fe_2O_3 in various modifications, 16-20% Al_2O_3, 8-13% SiO_2, 4-18% TiO_2, 4-12% $CaCO_3$ and minor amounts of oxides of V, P, Cr, Mn, Zn and Ca. The surface area was 15 m^2/g, the modifications contained free alkali bicarbonate and alkali metal carbonates. Six hydrotalcite like oxides were prepared from hydrotalcite like compounds MHT, (M = Mg, Ni, Co, Cu, Zn and Fe) synthesized according to [13] by sol-gel method. The precursors were prepared by co-precipitation from aqueous solution A containing nitrates of aluminum and of desired metal X (molar ratio X/Al = 1.5) with a basic solution B of NaOH and Na_2CO_3, dropwise added to deionized water at the room temperature under vigorous stirring, up to pH value between 10.7-11.2. The resulting gel (solid precipitate) was aged by stirring at 500 min^{-1}, at 80°C for 24 hours. Subsequently, the gel was washed with an excess of deionized water until neutral pH reaction of leachate and dried at 100°C for 12-16 hours. Finally, the as-prepared precursor was calcinated at 300°C for 4 hours in air in muffle furnace to get the corresponding metal hydrotalcite.

The prepared catalysts were characterized in terms of morphology and mesoporous structure. The surface area and pore volumes were measured by N_2 physical sorption using BET method in Quantachrome Autosorb iQ analyser.

The adsorbed amount of gas depends on the specific surface area, which is the sum of the internal surface of the pores and the available external surface of the particles. The value of the external surface depends on the size of the available pores, on the size of the particles (crystal), and on their shape. The basic textural characteristics of the prepared catalysts - specific surface area and pore structure are shown in Table 1, and for an example the isotherms of sorption for ZnHT catalyst in nitrogen are presented in Fig. 1.

Table 1: Basic textural characteristics of catalysts by BET analysis

Catalyst	Specific surface area S_{BET} [m^2/g]	C_{BET}	V_{micro} [cm^3/g]
CoHT	246	50.948	<0.001
FeHT	205	146.139	<0.001
NiHT	178	305.457	<0.001
CuHT	103	5070.380	<0.001
ZnHT	46	114.298	0.001
MgHT	33	226.416	<0.001

According to the literature data, the linear shape of C_{BET} isotherm at a relative pressure of 0.05 to 0.3 P/P_0, is typical for all mesoporous, macroporous and non-porous materials. C_{BET} constant of isotherm for most of non-porous, meso- and macroporous materials is usually in the range <30-150>. It matches well for our synthesized catalysts with Co, Zn, Fe (Table 1). Higher values of C_{BET} constant of isotherm were determined for catalysts with Mg, Ni and Cu, which would indicate the presence of micropores. The value of micropore volume was calculated according to the equation V_{micro} = intercept × 0.00155.

In the case of hydrotalcites of Ni, Fe and Co satisfactory values of specific surface area - in the range 180-250 m^2/g were reached. For example, the specific surface area of CoHT is greater than value 224 m^2/g, as it is stated in the literature. On contrary, the specific surface detected for MgHT and ZnHT was unexpectedly low. Despite the very low specific surface area of the synthesized catalysts – hydrotalcites MgHT and ZnHT achieve remarkable conversion efficiency and selectivity (see Table 2).

The differences in the values of the specific surface area may result from the particle size of the tested catalysts. The value of volume of micropores (V_{micro} equal 0.001 cm^3/g or less) indicates that the proportion of micropores in the materials is minimal. The highest determined value V_{micro} was in the following order: Zn > Mg > Co catalyst. Isotherm is convex in whole pressure range, so indicating in that way a weak sample-gas interaction. Hysteresis loop is minimal (see Fig. 1). This type of hysteresis is typical for flat aggregates of particles, which indicates that the prepared catalysts are not crystalline structures, but have layered structure and thus the character of hydrotalcite.

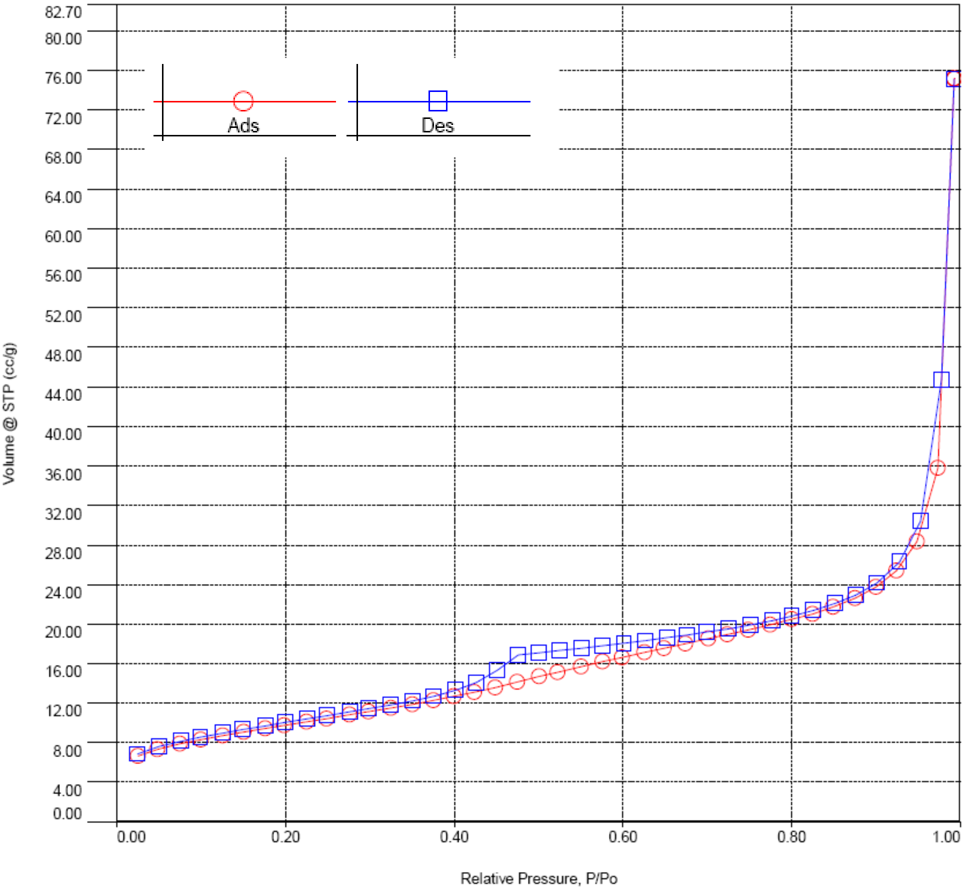


Figure 1: Adsorption-desorption curve of hydrotalcite ZnHT

TGA / DTA analysis (Fig. 2) was performed on the system Seiko DTA / TG Exstar 6300, in the temperature range 10-900°C, heating rate 5°C/min, N_2 100 mL/min. Progress TGA curve referred to the sustained release of water from the inter-layer space of hydrotalcite at 125 and 200°C. In the next step, in the temperature range 380-410°C, the cleavage of OH^- and CO_3^{2-} groups was detected. All samples were characterized by XRD analysis using STOE theta/theta analyzer equiped with CoKα radiation. The diffraction patterns of all the catalysts had typical hydrotalcite like structure (see Fig. 3).

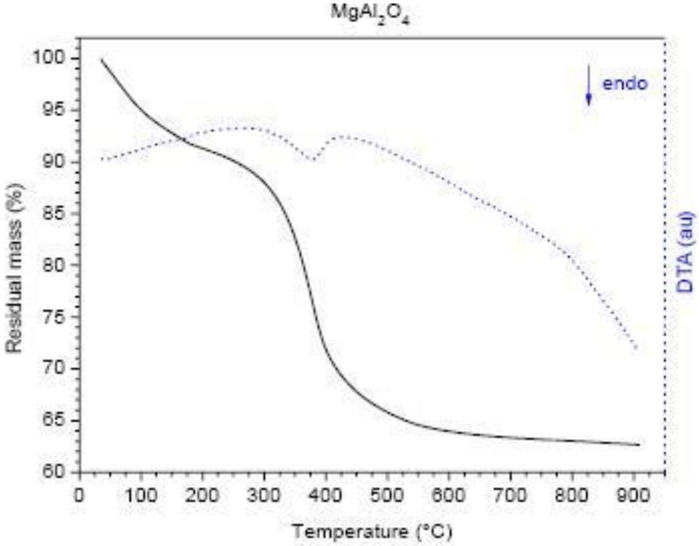


Figure 2: TC/DTA analysis of hydrotalcite MgHT

2.2 The procedure

For aldol condensation the model compounds furfural (F), p.a. and acetone (Ac), analytical grade (Mikrochem Pezinok) were used. Furfural is prone to oxidation, therefore, before the actual test, it was purified on a column with Al_2O_3. The experiments at temperature range 20-100°C were performed in a glass autoclave Buchi Ecoclave 1L. The reactants were used in a volume ratio (F:Ac) 1:9. For 25 ml of furfural 8 g of the catalyst was added. For the tests catalysed by MgO or hydrotalcite, the following conditions were selected: temperature of 20, 50, 100°C, the intensity of stirring 1000 min^{-1} and the pressure up to 1.0 MPa. The time of experiment varied from 3 hours to 24 hours. The samples, taken during the experiment, were filtered with a membrane filter Chromafil Xtra 0.45 µm. Liquid products were separated from the catalyst after the reaction by the centrifuge. The experiment at 140°C were performed in pressurized metal stirring autoclave Parr Instruments as batch experiment under N_2 atmosphere and at pressure 0.9-1.3MPa, for 4 hours. The tested weight ratio of catalyst/furfural was from 0.15 to 0.30. The performance of the catalysts was evaluated on the concentration of furfural in the reaction mixture and for the selectivity to the aldol products as follows:

$$furfural\ conversion\,(\% = \frac{moles\ of\ furfural\ reacted}{moles\ of\ furfural\ on\ input}$$

$$monomer\ selectivity\ (\%) = \frac{moles\ of\ monomer}{moles\ of\ reacted\ furfural}\,x\ 100$$

$$dimer\ selectivity\ (\%) = \frac{2\ x\ moles\ of\ dimer}{moles\ of\ reacted\ furfural}\,x\ 100$$

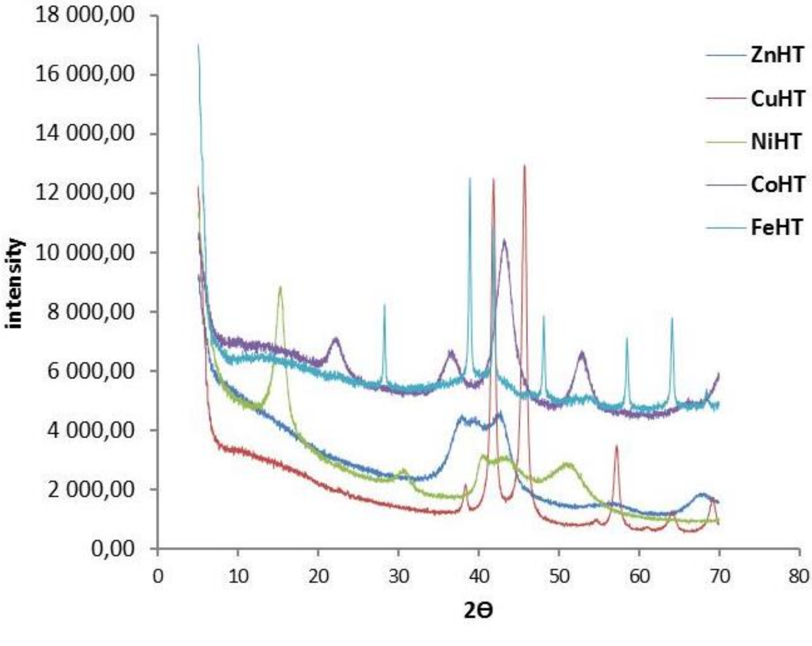


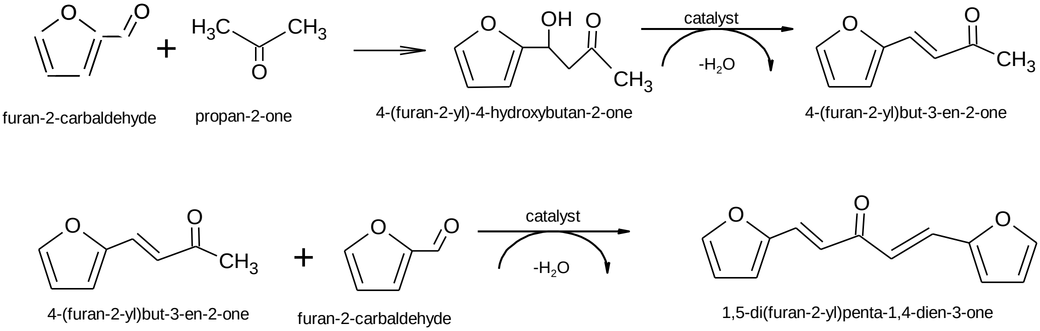
Figure 3: XRD patterns of tested HT powders

2.3 Analyses

The products of aldol condensation were separated by high-resolution capillary gas chromatography in a 30 m long columns with non-polar stationary phase DB-5. For identification of the separated isomers the available standard reference materials, published retention characteristics and mass spectrometry were used.

3. Results and discussion

The aldol condensation is easy performed in an organic solvent as with NaOH as a homogeneous catalyst. The AC reaction in the homogeneous phase is rapid, but it is associated with the formation of emulsions, necessity of neutralization of the reaction mixture, and is connected with the generation of waste. Preferably, the use of solid catalyst is circumventing the process of neutralization of a homogeneous catalyst. The disadvantage is the deactivation of active centers of the catalyst and the need for reactivation. The reaction of aldol condensation furfural with acetone proceeds according to the Scheme1.



Scheme 1: Aldol condensation of furfural and acetone over basic heterogeous catalyst

In the first step of reaction one molecule of furfural reacted with one molecule of acetone to produce 4(2-furanyl)-4-hydroxy-2-butanone (FAc_{ol}), which is then dehydrated to 4(2-furanyl)-3-butene-2-one (FAc). In the consecutive step a molecule of FAc reacts with a molecule of furfural (F) to give 1,5bis(2-furanyl)-1,4-pentadiene-3-one (F_2Ac). A possible side reaction is condensation of two molecules of acetone to diacetone alcohol $C_6H_{12}O_2$ (DAA), followed by dehydration to mesityl oxide. In the tests the basic type heterogeous catalysts and hydrotalcite like layered double hydroxides was compared. Table 2 contains the results of furfural conversion and selectivity to FAc_{ol}, FAc and F_2Ac over basic magnesium carbonate, magnesium oxide and brown mud. Basic magnesium carbonate had shown low activity, furfural conversion reached only 16.5%. Dehydration FAc_{ol} was at 100^{o}C very low. The slightly higher activity had calcinated brown mud from Al_2O_3 production. The conversion of furfural at 100°C was 48.1% and the selectivity to F_2Ac was very low.

Pure MgO contain strong basic sites, predominantly O^{2-}, medium (oxygen in $Mg^{2+}O^{2-}$ pairs) and weak (OH^{-}) basic centers. The distribution of active basic sites depends strongly on the temperature of calcination. The increase of the calcination temperature drastically decreased the density of strong base sites and let to a lesser extent that of weak OH^{-} groups, while slightly increased that of medium-strength base sites [9]. Most active during the series of tests was MgO catalyst prepared by calcination of precursor - basic magnesium carbonate, at 450ºC. It was already active at temperature of 20°C. Higher temperatures facilitate the condensation reactions of aldol condensation, as the dehydration step is more rapid at higher temperatures. Figure 4 shows the course of aldol condensation of furfural and acetone at 50°C, the intensity of agitation 1000 min^{-1}. The lines show a quick decrease of concentration acetone and furfural. The selectivity to FAc_{ol} passes through maximum after 1.5 hour of reaction and after 4 hours FAc_{ol} was not detected in the reaction mixture. The reaction take place consecutively, one molecule of furfural reacted with one molecule of acetone to produce FAc and then second molecule of furfural reacted with one molecule of acetone to F_2Ac. The reaction using MgO was carried out at temperature 20, 50 and 100ºC.

Reaction rate of aldol condensation of acetone and furfural increases considerably with rising of temperature (see Fig. 5). FAc_{ol} is absent in reaction products at temperature 100ºC due its fast dehydration to FAc. The diacetone alcohol as possible side product was not detected in the reaction products.

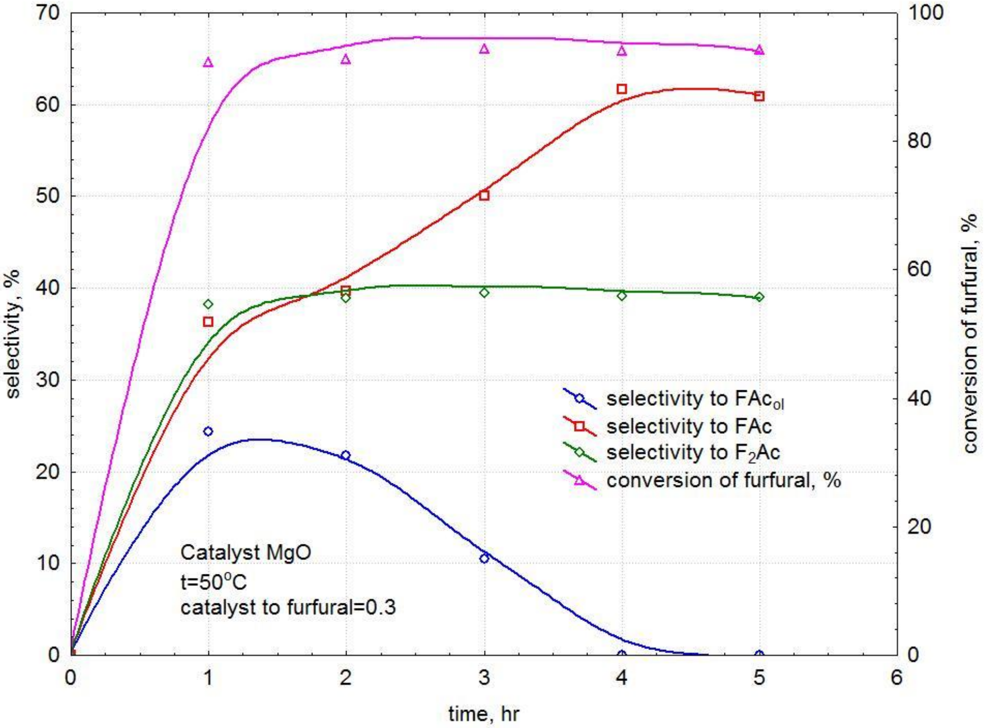


Figure 4: Aldol condensation of furfural and acetone on MgO catalyst at 50ºC

Table 2: Comparison of furfural conversion and selectivity over basic magnesium carbonate, MgO and brown mud catalysts

Catalyst	*T*, °C	Reaction time, hours	Weight ratio of catalyst / F	Conversion of F, %	Selectivity to FAc$_{ol}$, %	Selectivity to FAc, %	Selectivity to F$_2$Ac, %
$4MgCO_3 \cdot Mg(OH)_2 \cdot 4H_2O$	100	4	0.30	16.5	13.2	13.2	7.3
MgO	20	24	0.30	59.8	0	55.9	15.3
MgO	50	5	0.28	94.2	0	79.5	50.9
MgO	100	5	0.28	94.5	0	79.2	46.1
Brown mud	100	4	0.30	48.1	1.8	27.8	3.7

F - furfural; FAc$_{ol}$ - 4(2-furanyl)-4-hydroxy-2-butanone; FAc - 4(2-furanyl)3-butene-2-one; F$_2$Ac - 1,5bis(2-fyranyl)1,4-pentadien-3-one

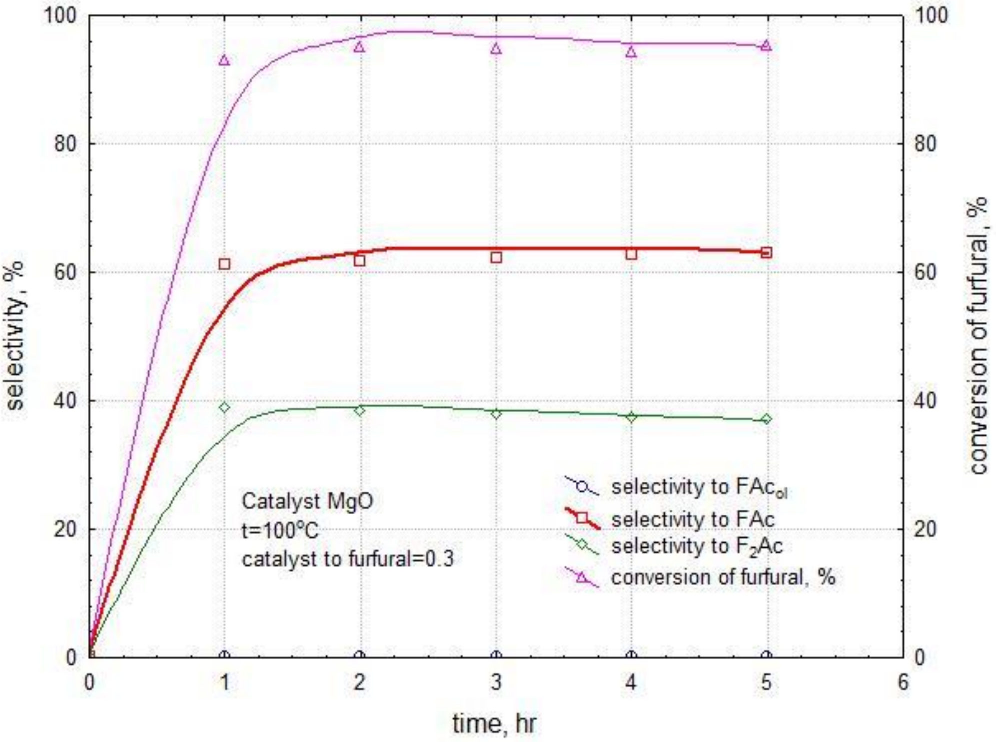


Figure 5: Aldol condensation of furfural and acetone on MgO catalyst at 100°C

MgO catalyst after the reaction was coloured brown (see Fig. 6) and in repeated aldol condensation was practically inactive. On the surface of the catalyst were adsorbed reaction products which may have been partially taken up in ethanol and acetone. The calcinated MgO catalyst was not fully regenerated, probably due the changes in surface area and structure.

Figure 6: Photo of MgO catalyst, from left to right fresh MgO, MgO after aldol condensation, MgO after calcination

Hydrotalcites have similar distribution of basic catalytic centers as MgO. It was compared the catalytic performance of industrially produced hydrotalcite Mg-Al and synthetically prepared hydrotalcites.

Table 3: Comparison of furfural conversion and selectivity on specific products by different catalysts of calcinated hydrotalcite catalyst

Catalyst	Temperature, °C	Reaction time, hours	Weight ratio of catalyst / F	Conversion of F, %	Selectivity to FAc_{ol}, %	Selectivity to FAc, %	Selectivity to F_2Ac, %
Hydrotalcite*	100	4	0.28	93.8	4.6	41.2	25.7
Hydrotalcite**	100	4	0.28	91.6	0	59.6	28.2
ZnHT	140	4	0.29	100	0	86.0	12.2
ZnHT	140	4	0.15	55.2	8.2	62.2	8.2
MgHT	140	4	0.30	100	0	81.7	14.3
MgHT	140	4	0.15	39.4	10.5	43.9	8.9
CoHT	140	4	0.28	100	0	74.5	16.7
NiHT	140	4	0.29	100	0	78.0	31.5
FeHT	140	4	0.30	100	0	79.7	15.5
CuHT	140	4	0.30	49.8	6.1	77.4	6.3

F - furfural; FAc_{ol} - 4(2-furanyl)-4-hydroxy-2-butanone; FAc - 4(2-furanyl)3-buten-2-one;
F_2Ac - 1,5bis(2-fyranyl)1,4-pentadien-3-one;
**industrial HT Mg/Al=1.5, **hydrated industrial HT Mg/Al=1.5*

The industrial hydrotalcite with ratio Mg/Al of 2.2 showed a high conversion of furfural and selectivity to furfural FAc was higher in the case of in-situ re-hydration of catalyst. Hydrotalcite catalyst during the reaction changed color from white to intense dark orange. Part of the reaction products remained adsorbed on the surface, subsequent washing with acetone was only partially successful. After calcination of the catalyst, the color changed to white, and the activity was restored.

The comparative tests with six MHT catalysts with selected metals (M= Mg, Zn, Ni, Co, Cu and Fe) were studied at 140°C. All types, except of CuHT reached 100% conversion of furfural and high 74.5-86.0% conversion to FAc (see Fig. 7). The best results (86.0 and 81.7% selectivity to FAc) were obtained in case of Zn and Mg hydrotalcites despite the low determined specific surface by BET method. On the contrary, the highest selectivity regarding F_2Ac was observed with the catalyst Ni and Co hydrotalcites with the highest specific surface (see Table 3).

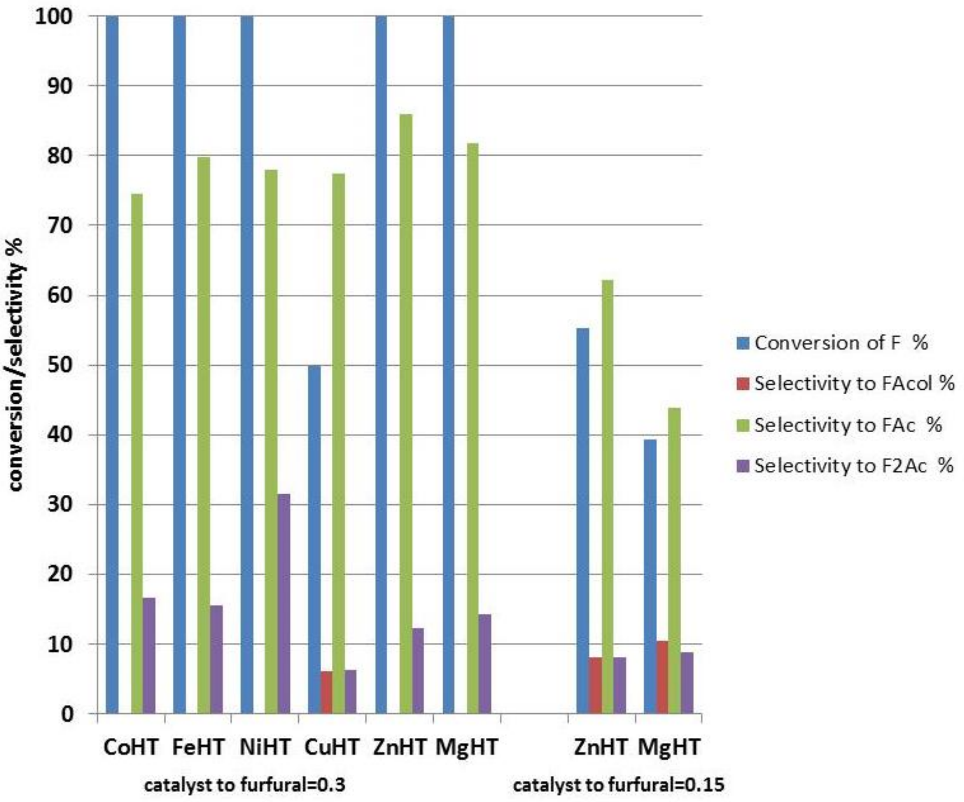


Figure 7: Comparison of furfural conversion efficiency and selectivity of the catalysts MHTs for targeted products

As a critical parameter for high conversions has shown the ratio catalyst to furfural close to 0.3. Comparable results are given in the literature [10], where in the aldol condensation of hydroxymethylfurfural and acetone 81% selection to FAc and 10-11% selection for F_2Ac, at ratio cat/F equal 0.3, was reached by spinel-like catalyst prepared by via co-precipitation with carbon black. At a lower cat/F ratio (0.15) the conversion in our tests was only half of the value. The amount of the catalyst was not sufficient for acetone furfural aldol condensation. In such cases, the primary condensation product FAc_{ol} remained detected (selectivity of 4.0- 10.2%).

4. Conclusion

Six catalyst based on hydrotalcites were prepared and tested for aldol condensation of furfural and acetone. Five of synthesized MHT catalysts showed complete conversion of furfural, satisfactory high selectivity to C_8 products (up to 86%) and the promising selectivity to C_{13} products. The reaction conditions were as follows: temperature of 140°C, pressure 1.3 MPa and catalyst/furfural ratio of 0.3. The best results were obtained with Zn and Mg hydrotalcites, with specific surface S_{BET} 46 and 33 m^2/g, respectively. On the contrary, low conversion showed Cu aluminate.

For the other types of tested catalysts, in terms of conversion and selectivity the highest effect showed MgO and in-situ hydrated hydrotalcite of ratio Mg/Al = 2.2. The problem with using hydrotalcite catalyst are their deactivation by strong adsorption of the reaction products on the catalyst surface. By calcination at a temperature of 450°C, the activity was restored. The composition of reaction mixture depends on the activity of the catalyst active sites.

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KATALITIČKA KONVERZIJA PIROLITIČKIH BIOULJA U GORIVA

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Sažetak

Provedena je aldolna kondenzacija modelnih tvari furfurala i acetona pomoću odabranih konvencionalnih katalizatora. Katalitička aktivnost MgO uspoređena je s industrijskim hidrotalcitom te nizom hidrotalcita priređenih u laboratoriju.

$Si{\times}MAl_2O_4$ hidrotalciti (M = Mg, Zn, Ni, Co, Cu, Fe) pripravljeni su sol-gel postupkom pri niskoj temperaturi kalciniranja od 300 °C. Svojstva katalizatora ispitana su XRD i BET metodama pri čemu je ustanovljena mezoporozna struktura. Aldolna kondenzacija provedena je u tekućoj fazi pretežito u atmosferi N_2, u temperaturnom rasponu 25-140 °C pri povišenom tlaku. Glavni kondenzacijski proizvodi su C_8 FAC monomer i C_{13} F_2Ac dimer. Prvi intermedijer FAc_{ol} lako se dehidrira pri višim temperaturama. Postignuta je pretvorba furfurala (F) u C_8 produkte (FAc) u rasponu od 55,9 do 94,5 % uz selektivnost 41,0 - 79,5 %.

U usporednim testovima provedenim na 140 °C s MHT hidrotalcitima, najbolji rezultati dobiveni su u slučaju Zn i Mg hidrotalcita unatoč njihovoj maloj specifičnoj površini. Visoka selektivnost prema F_2Ac uočena je kad su kao katalizatori korišteni Ni i Co hidrotalciti specifične površine 178 i 246 m^2/g. Kao ključni parametar za postizanje visokih konverzija utvrđen je omjer katalizator / furfural približno 0,3.

Ključne riječi: *aldolna kondenzacija, hidrodeoksigenacija, hidrotalcit, furfural, aceton, MgO*

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