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Concepts of modern technologies of obtaining valuable biomass-derived chemicals

Koncepcje nowoczesnych technologii pozyskiwania cennych związków chemicznych z biomasy

Abstract

In this paper, we present the review of modern technologies for obtaining valuable biomass-derived chemicals, such as furfural, levulinic acid, adipic acid, dihydroxyacetone, lactic acid and acrylic acid. We have included our own research approach using the nano-design of zeolites for the dehydration of lactic acid into acrylic acid.

Keywords: biomass, lignocellulose, zeolites, lactic acid, acrylic acid, adipic acid, furfural, levulinic acid

Streszczenie

W niniejszej pracy przedstawiono przegląd nowoczesnych technologii uzyskiwania cennych związków chemicznych pochodzących z biomasy, takich jak furfural, kwas lewulinowy, kwas adypinowy, dihydroksyaceton, kwas mlekowy i kwas akrylowy. Zaprezentowano również własne podejście badawcze obejmujące projektowanie w skali nanoskopowej zeolitów do odwadniania kwasu mlekowego do kwasu akrylowego.

Słowa kluczowe: biomasa, lignoceluloza, zeolity, kwas mlekowy, kwas akrylowy, kwas adypinowy, furfural, kwas lewulinowy

1. Introduction

Nowadays, crude oil and natural gas are the main sources for the production of fuels and feedstock chemicals. These resources are limited and the application of (renewable) alternatives will be needed in the future to sustain the progress of mankind. A major challenge of society research is to create fuels and chemical intermediates from available and renewable materials that do not compete with food crops for water or fertilizers [1].

Biomass is the one exceptional sustainable source for chemicals and fuels [2]. The U.S. Department of Energy has predicted that 25% of chemicals and 20% of transportation fuels will be prepared from biomass in the next two decades [3]. The main objective of the European Union, as well as other countries, is to make every effort to reduce global warming caused by the processing of fossil fuels. All attempts to protect the environment from the negative effect of economic development are included in the so-called climate packet, which describes the reduction of greenhouse gas emissions as well as developing and implementing efficient and modern technologies [4, 5]. In addition, quantitative targets have been introduced in EU countries until 2020, the so-called "3 x 20%". It involves a reduction of greenhouse gases by 20% compared to 1990, a reduction of energy consumption by 20% by 2020 and an increase in the use of renewable energy resources to 20% [6]. Recently, technologies using organic waste as a raw material have been dynamically developing, as well as biomass for energy production, which constitutes 67% of primary energy, of which 48.1% is lignocellulosic biomass [7]. As a result of conducting research and creating technologies for receiving products from biomass, a new branch of industry was established – biorefinery [4, 5, 8, 9]. In this perspective, heterogeneous catalysis possesses have a tremendous potential for overcoming scientific and engineering barriers, thus rendering feasible and economic bio-based conversion routes [10]. Biomass does not allow a direct extrapolation of petrochemical technologies. The abundant presence of oxygen makes biomass-derived molecules soluble in water, of low volatility, highly reactive, and prone to decomposition at high temperature. In the literature, numerous pathways (dehydrations, oxidations, hydrogenations, hydrogenolysis, isomerizations) are proposed to produce a large number of molecules [6,11]. Nevertheless, transforming these theoretical conversion routes into industrial reality is not straightforward.

2. Lignocellulosic biomass

Biomass from woody plant materials (e.g. corn and wood wastes, grass etc.) is a promising biorenewable feedstock [12]. However, the use of biomass for feedstock production requires a sequence of chemical conversions, which is blocked by the main building: carbohydrates. Recently, global efforts have been underway to convert plant cell walls (which are collectively called lignocellulosic biomass) to biofuels for transportation needs [13–15]. At first, this requires breaking down the lignocellulose nanostructure of biomass. Lignocellulose is built from cellulose crystals embedded in hemicellulose sugars and lignin polyphenols (Fig. 1) [16].

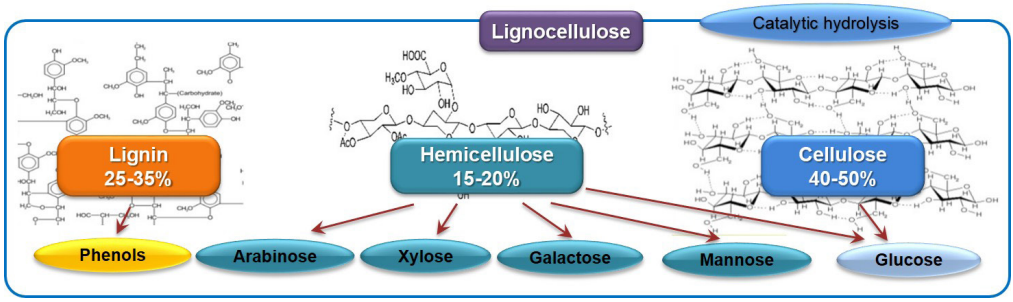

Fig. 1. The chemical composition of lignocellulose and the main products of catalytic hydrolysis [17]

Cellulose is the most abundant and important constituent in plant cell walls. Its crystal structure and complex network with other carbohydrate polymers are key factors determining the mechanical strength and degradability of plant cell walls [18, 19]. Another constituent is lignin, which is removed from wood meal by the paper industry. Lignin is one of the three main biopolymers, together with cellulose and hemicellulose, which builds the cell walls of plants. Lignin consists of aryl ethers, irregularly connected by a variety of linkages [20]. Lignin is taken as a base material to manufacture biopolymers by conventional polymer techniques. A further application field is agriculture; lignin products can be the basis for delayed-action fertilizers, which release nutrients slowly or serve as support for the production of humus in the soil. In view of its chemical composition, lignin is a rich raw material for aromatic (phenolic) compounds with a high added value. In 2004, the pulp and paper industry alone produced 50 million tons of extracted lignin, but only approximately 2% of the lignin available is used commercially, with the remainder used as a low-value fuel [21]. The extraction of lignin from wood is especially difficult.

There are a few explanations for the difficulty in extracting lignin [22]: (i) strong covalent bonds exist between lignin and carbohydrates, (ii) lignin has a high molecular weight and possibly forms a three-dimensional network [23], (iii) hydrogen bonds and physical phenomena, such as solid solution, may be involved in the retention of lignin in the wood-fiber wall. Pretreatment of lignocellulose requires extreme conditions (e.g. temperature, pressure, and reagent, which are toxic for environment). Cellulose is building up the structural substance of unlignified cell walls and consists of fibrous macromolecules based on anhydroused *d*-glucose units. Single polysaccharide chains are hydrogen bonded and build microfibrils, which are resistant to hydrolysis. A high degree of polymerization causes orientation, elasticity and a large tensile strength of this carbohydrate. Hemicellulose is also a polysaccharide (such as arabinose, glucose, galactose, mannose and xylose) and consists of different monomers building a random, amorphous structure. Arabinose is aldopentose and mainly a component of hemicelluloses and pectins [17, 23, 24].

The general scheme (Fig. 2) illustrates the processes of fuels, chemicals and energy production from the biomass. The most crucial for the environment are three first steps (Fig. 2, dark blue color): (i) lignocellulose conversion (e.g. via dissolution by ionic liquids or hydrothermal gasification by Ru-catalysts), (ii) methanation by Ni-catalysts, (iii) selective conversion into chemicals (via isomerization, dehydration, oxidation etc. by e.g. zeolites).

All these three classes of processes require various types of catalysts, but they are connected and depend on each other, e.g. methanation and conversion into chemicals processes depend strongly on products mixture of lignocellulose conversion.

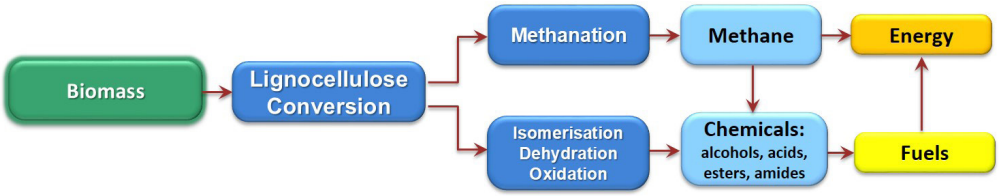

Fig. 2. Scheme illustrating the processes of biomass conversion

3. Zeolites in biomass conversion

Zeolites are very promising materials for biomass conversion into lactates, acrylates and may be valuable products derived from biomass. Zeolites, microporous and crystalline aluminosilicates, are effective catalysts in many applications [6]. The different zeolitic materials are characterized by a variety of micropore structures featuring specific sizes, shapes, and connectivity (Figure 3) as well as possibility to tune acid/base properties. Due to the ability to catalyze many types of hydrocarbon reactions zeolites are ideal candidates for the production of chemicals from biomass [25, 26]. Zeolites are effective three-dimensional supports for active nanoparticles. However, industrial performance and selectivity of microporous zeolites to the desired chemicals at the industrial scale is far from being optimal due to the limited access to the micropores with active basic/acid sites or nanoparticles and diffusion limitations. From the other hand ordered microporous metallosilicates containing auxiliary mesoporosity, have shown improved performance compared to purely microporous zeolites in a wide range of catalyzed reactions. The introduction of mesopores into the microporous zeolite network by selective demetallation has been shown to lead to strong variations in performance and changing the access to the active sites, enhancing catalyst selectivity and activity [27, 28]. Mesopores introduction is known to depend on internal properties of the zeolites (framework type and composition) resulting in a different distribution of mesopores. Structural origin increased mesopore surface area. However, up to now, knowledge about the demetallation process on the atomistic level is almost not existent. One of the major obstacles to unimproved understanding is the difficulty in modeling a complicated structure of zeolites mesopores.

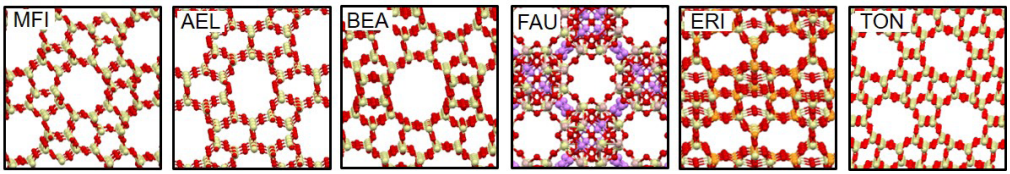

Fig. 3. Differences in natural micropores in various zeolite structures

The mesoporous structuring of conventional zeolites by post-synthetic modification is one of the most efficient means of enhancing their performance in diffusion-limited reactions [6]. The extent and distribution of the introduced mesopores have experimentally been observed to depend strongly on the intrinsic properties of the zeolite [29]. As the catalytic benefits of mesoporosity in zeolites primarily derive from an enhanced molecular transport, the extent and distribution of mesopores created within the zeolite crystals can be expected to have critical implications. Therefore, it is important to understand the structure of micro- and mesopores and their role in: (i) transport properties of adsorbates, (ii) distribution of metallic nanoparticles. Evidently, the molecular-level description of the synthesis and properties of mesoporous zeolites would be highly valuable to rationalize the demetallation behavior of zeolites. However, the complex structure of zeolites, particularly when integrating non-periodic mesopores, and the difficulty in accounting for their interaction with aqueous media, comprise major barriers to an improved theoretical understanding, which remains limited. The framework defects are expected to have an essential role in the mesopores formation process and give good perspectives to understand demetallation. One of the major obstacles to an improved understanding is the difficulty in modeling the complex and non-periodic structure of mesopores in zeolites. Several groups were tackled ZSM-5 crystal structure and model adsorption processes using both cluster and periodic DFT calculations [30–36].

The original acid/base properties can also be precisely modified to match the requirements of the target reaction. By depositing metal nanoparticles, additional functionalities can be integrated into one material. The use of a zeolite as a carrier for the metal phase is expected to be very favorable for obtaining a material with desirable properties. The mesopore zeolites have an even larger external surface into which the metal phase can be deposited, thus achieving higher dispersion, and the closer proximity of the metal and acid/base site in the solid with respect to the corresponding micropore zeolite. Zeolite-based catalysts have not been extensively applied in biomass conversion so far and never in mesoporous form, but the results are primarily promising [37]. Micro- and mesoporous zeolites are attractive and suitable catalysts for liquid-phase conversions taking into account their water compatibility and the benefits provided by a porous system for the transport to/from the active sites of typically highly viscous biomass-derived compounds. However, more detailed studies on the structure of active sites and metallic nanoparticles carried in zeolites, as well as the mechanism of biomass conversion into chemicals, are necessary.

4. Selected compounds from biomass

4.1. Fructose: aldo-keto isomerization of glucose

Acquiring fructose from biomass, due to low raw material costs, is an interesting pathway for obtaining a variety of useful monomers. One of the methods of fructose production is the aldol-keto isomerization from biomass-derived glucose. Figure 4 shows the reaction pathways of glucose and fructose [38]. Fructose may be an intermediate in subsequent

transformations to HMF or lactic acid. One of the concepts of performing fructose reactions is to obtain a catalyst with Lewis active centers. For this purpose, the Sn-Beta zeolite was designed, which has the ability to convert glucose to fructose. The presence of additional sodium cations in the structure enables the glucose reaction to mannose [38,39]. In order to confirm the effectiveness of the above catalyst, theoretical studies were carried out using the DFT method. Reaction barriers for partially hydrolyzed and fully coordinated tin at specific locations using energy distribution analysis were tested. In addition, Sn was replaced with other metals such as Ti, Zr, V, Nb, Si and Ge. It has been found that Sn and Zr are metals that have the lowest energy barrier for glucose isomerization. It also depends on the physical properties of metals and the basicity of the centers of active oxygen atoms associated with the metal atom [40]. Another example of the zeolite usage in the glucose isomerization reaction is Y, H-beta and H-USY zeolite. The reaction occurs in two stages in various solvents. The first step is the reaction of the isomerization of glucose in methanol to produce methyl-fructoside, followed by hydrolysis to fructose after the addition of water. The reaction takes place at 120°C for 1h involving the above-mentioned catalysts. As a result of the process, the product was obtained with the highest yield of 55% using H-USY. Conducting this process at higher temperatures leads to a product like methyl levulinate [41].

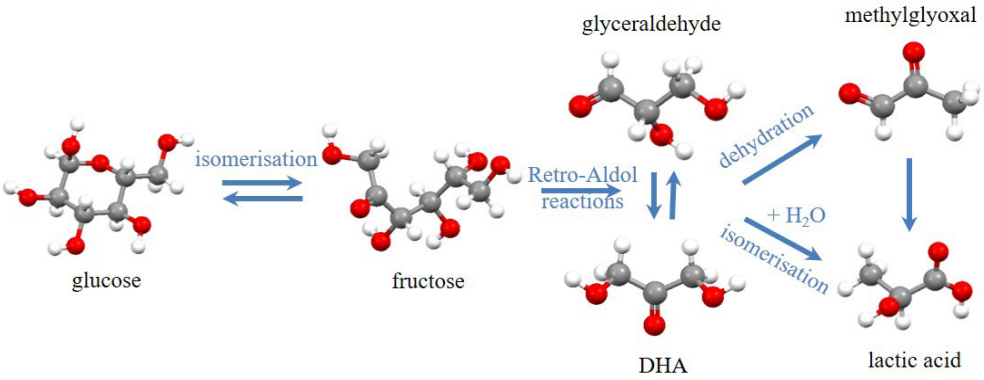

Fig. 4. Scheme of reaction pathways of glucose and fructose

The process of glucose isomerization to fructose was also carried out on NaY zeolite with magnesium cations incorporated into zeolite (0-15 wt.%). It was observed that the increase in magnesium content in the structure (10 and 15% by weight) significantly improves the degree of glucose conversion (6-49%). However, the yield of fructose was only about 32% [42]. Tests were also carried out with the zeolites A, X, Y and hydrotalcites. Alkaline cations: Na^+, K^+, Cs^+, Ca^{2+}, Ba^{2+} were introduced into the structure of these materials on the basis of ion exchange. The process was carried out in an aqueous environment at 95°C, at 8 bar. The best among the tested zeolites were NaX and KX zeolites with a selectivity into fructose of about 90% and a conversion of glucose of around 10-20% [43].

The further essential processes of fructose transformation into glyceraldehyde (GLA) and dihydroxyacetone (DHA) are retro-aldol reactions.

4.2. 5-hydroxymethylfurfural and furfural

The production of 5-hydroxymethylfurfural (HMF) and furfural should be essential for the industry since both compounds are used as a substrate in several syntheses. HMF is formed by the dehydration process of different aldoses from the hydrolysis of biomass [44]. HMF can be converted to a range of derivatives having potential applications in the biofuels, polymer, and solvent industries. There are several promising studies concerning catalytic processes of HMF production from biomass over a range of catalysts from hydroxyapatite supported chromium chloride, metal chlorides up to ZSM-5 [45–47].

Examples of reactions catalyzed with the corresponding zeolites are given in Figure 5. One of the zeolites used in the production of HMF is the dealuminated BEA zeolite, which has been formed by the calcination of the $NH4^{+}$BEA form at a temperature above 700°C or the treatment of this material with steam in 500°C. The Si-O-Al bonds inside the zeolite structure are broken, resulting in an increase of Lewis active centers. The calcinated BEA zeolite has been used in the reaction of the conversion of glucose to HMF with a selectivity of 55% at a 78% conversion [48]. Another possibility is to conduct the process of HMF production from glucose in a 1-butyl-3-methylimidazolium chloride solvent with BEA zeolite (Si / Al = 25) as a catalyst. The catalyst has the highest activity, resulting in HMF with a 50.3% yield at a 80.6% glucose conversion at 150°C for 50 minutes [49]. The HMF production process is also possible in the ionic liquid 1-butyl bromide-3-methylimidazolium solvent in MOR zeolite [50]. Also, the conversion of glucose to HMF takes place with the participation of catalysts such as SAPO-34 [51], H-, Fe-, Cu-ZSM-5 [52] or over the hierarchical Zr-Al-BEA [53].

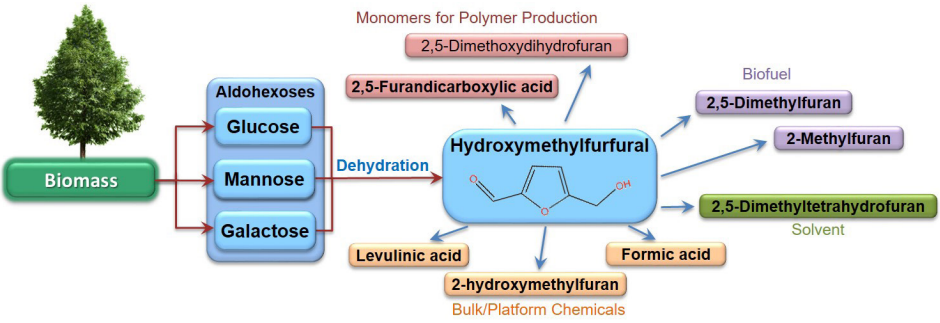

Fig. 5. Scheme illustrating the targeted product (HMF) from biomass-derived feedstocks and its usage as a substrate in further synthesis into valuable chemicals [44]

Additionally to the conversion of biomass to HMF, it is also important to obtain furfural. Furfural is one of the strategical and ultimate industrial intermediates [54]. Furfural is converted into furfuryl alcohol, methylfuran and furan via metal-catalyzed hydrogenation, reduction and decarbonylation, respectively (see Figure 6). Also, different valuable products are produced from furfural: α-furfuryl alcohol, tetrahydrofurfuryl alcohol, methylfurfuryl alcohol, 5-dimethylaminomethylfurfuryl alcohol, furoic acid, furfurylamine, methylfuran, 2-acetylfuran and 2,5-dimethoxydihydrofuran.

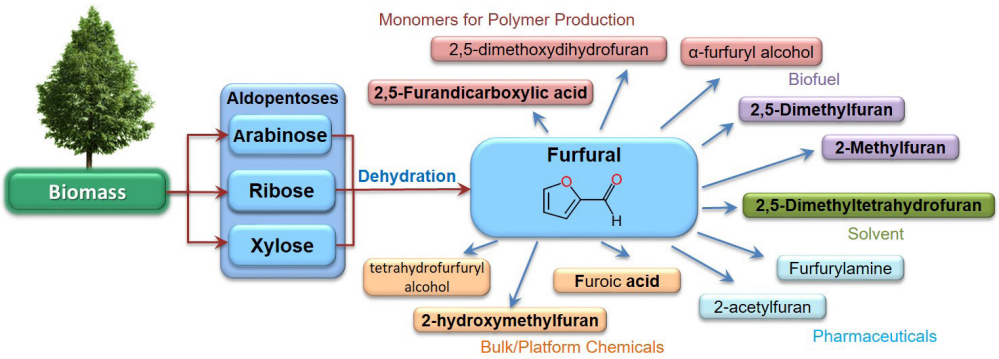

Fig. 6. Scheme illustrating the targeted product (furfural) from biomass-derived feedstocks and its usage as a substrate in further synthesis into valuable chemicals

The reaction of C5 monosaccharides (xylose, arabinose, ribose derived from corn fiber) to furfural using H-beta zeolites, sulfuric acid (VI) and H-mordenite has been carried out. The furfural has been obtained with yields of 62, 55 and 44% respectively, using H-beta, H-mordenite and sulfuric acid. The H-beta zeolite has been found to be the most active due to the presence of Brönsted and Lewis centers (respectively at a ratio of 1.66). The H-beta catalyst gives a bifunctional effect: isomerization (due to the presence of the Lewis center) and dehydration (presence of the Brönsted center) of monosaccharides into HMF [54]. Dumesic et al. developed a reaction to obtain HMF from xylose, fructose and glucose using various catalysts. Their process had been carried out in γ-valerolactone at 175°C. Catalysts that were used were γ-Al2O3, Sn-beta, Sn-SBA-15, H-ZSM-5, zirconium sulfate, 0.02M sulfuric acid (VI), Nafion-SAC-13, sulfonated carbon, H-beta, Amberlyst 70, SBA-15 functional with propylsulfonic acid. From all tested catalysts, H-mordenite has the highest activity: in the case of glucose conversion (97%), HMF has been obtained with a yield of 32% and 36% for fructose at a 100% conversion rate [55].

A process of hydrolytic hydrogenation of arabinogalactan from hemicellulose into 5-hydroxymethylfurfural and furfural in the presence of a modified Ru-USY zeolite (Si/Al = 15 and 30, 1-5% ruthenium) has also been developed [56]. Another example is the usage of H-ZSM-5 zeolite in the dehydration of xylose to furfural. The process was carried out in the temperature range of 140-220°C. The highest selectivity was obtained at 200°C [57]. The other zeolites, such as SAPO-34 zeolites [58] and K-BEA [59], have the ability to carry out this reaction. Zhang et al. conducted a process of glucose conversion on BEA zeolites (ion exchange Fe-BEA, Sn-BEA, Zr-BEA). A furfural and HMF were obtained as by-products. Sn-Beta zeolite showed the highest activity, giving a product with a yield of 69.2% [60].

4.3. Levulinic acid and γ-valerolactone

Levulinic acid is one of the platform molecules used as a precursor for pharmaceuticals, plasticizers, and various other additives. It can be obtained through hydrolysis/dehydration of aldohexoses such as glucose and fructose, or hexose-containing polymers like starch and cellulose.

Levulinic acid was obtained as a result of glucose, starch and cellulose conversion in a hydrothermal process using Ga-MOR zeolite [61]. The process lasted for 6 hours at 175°C with a yield of 59.9%. Amin et al. have developed a hybrid catalyst containing chromium chloride and an HY zeolite. As a result of the reaction at 145.2°C for 146.7 min., they obtained a product with a yield of 55.2% [62]. Another example is the dehydration of glucose using MFI zeolite with different silicon module (Si/Al = 25, 30, 80, 120, 260). This process was carried out at 180°C for 8 hours. The MFI zeolite with the silicon module 30 has been found the most active; the product obtained in this case had a yield of 35.8% [63]. They also developed a number of Fe-HY catalysts with various percentages of iron (5, 10, 15%). Among the above catalysts, the 10% Fe-HY catalyst showed the highest catalytic efficiency of around 62% [64,65]. Levulinic acid (LA) has also been obtained by the conversion of xylose in the presence of hot steam using alkaline zeolite catalysts. Zeolite Y was treated with a sodium base with various molar concentrations (0.05 M and 0.25 M). The dealuminated Y zeolite, 0.25 M NaOH proved to be the most effective catalyst. The product was obtained with a yield of 30.4% and a conversion of 84.3%. The process was carried out for 3 hours at 170°C [66]. Zeolite LZY has also found application in the catalytic dehydration of fructose. The process was carried out in a batch reactor at 140°C for 15 hours. From 1 g of fructose, 0.432 g of levulinic acid has been obtained [67].

The γ-valerolactone (GVL) is another biomass-derived chemical compound - a potential fuel and green solvent. The γ-valerolactone can be obtained from furfural by the hydrogenation process at 120°C in a 2-butanol solution on Zr-BEA and Al-MFI catalysts [39,68-70]. GVL is also produced via hydrogenation reaction from levulinic acid. Other important chemicals like 1,4-pentanediol or 2-methyltetrahydrofuran can be obtained by chemoselective hydrogenolysis of GVL.

4.4. Adipic acid

Adipic acid is used in the production of nylon, PVC and polyurethanes and its production is about 2.5 MTon/year. Adipic acid is produced from a mixture of cyclohexanol and cyclohexanone, oxidative cleavage of cyclohexene using hydrogen peroxide or by the hydrocarboxylation of butadiene [71]. Adipic acid has traditionally been produced from various petroleum-based feedstocks (e.g., phenol, benzene, and cyclohexane), but shifts in the hydrocarbon market have resulted in the virtual elimination of phenol as a feedstock. In recent years, cyclohexane-based processes have accounted for about 93% of the global production capacity. Two steps are involved in ADA production: 1) oxidation of cyclohexane to produce KA oil (cyclohexanone and cyclohexanol) and 2) nitric acid oxidation of KA oil to produce adipic acid.

Recently, start-up companies such as Rennovia, Verdezyne, BioAmber, Celexion, and Genomatica have developed bio-based routes to produce adipic acid. Rennovia's patented a two-step process for the production of bio-based adipic acid from glucose:

(i) a selective catalytic oxidation of glucose to glucaric acid

(ii) a selective catalytic hydrodeoxygenation of glucaric acid to adipic acid (see Figure 7).

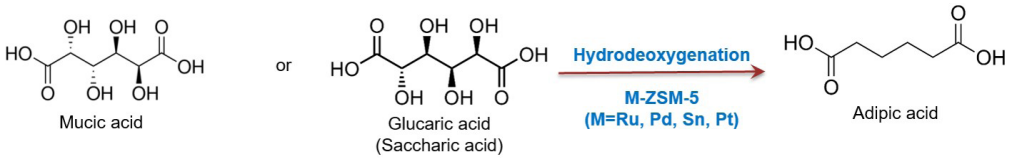

Fig. 7. Scheme illustrating the targeted product (adipic acid) from biomass-derived feedstocks (glucaric acid)

Two basic motivations for considering alternative biomass feedstock sources for the production of ADA are: 1) in the long term, they could be less expensive to produce than conventional methods using crude oil derivative cyclohexane and 2) societal demands for producing industrial chemicals via 'sustainable' methods or technology-specific market demand that results in requirements for producing ADA from bio-chemical resources. Potential catalysts for hydrodeoxygenation are metal (Ru, Pd, Sn, Pt) on ZSM-5.

4.5. Dihydroxyacetone

A new chemocatalytic technology for the continuous oxidation of glycerol (GLY) to dihydroxyacetone (DHA) in the gas phase has been developed. This process takes place over the Fe-MFI catalyst in the presence of molecular oxygen. The reaction was carried out in a fixed bed reactor. Activation of the steam generator at 600°C shows dispersed iron in the form of cations and FeOx clusters, which guarantee a product efficiency of 50% [72]. A method for converting dihydroxyacetone to C_1-C_4 alkyl lactate has also been developed. The process was carried out using MFI, MOR, FER, BEA zeolites with gallium particles. The Ga-FAU proved to be the most active, giving a product, such as n-propyl and n-butyl lactate and ethyl lactate [73]. Another possibility is the reaction of dihydroxyacetone into ethyl lactate in a Ga-USY catalyst [74].

4.6. Lactic acid / alkyl lactates

Developing efficient catalysts for the conversion of bio-renewable feedstocks to a selected key chemical, such as lactic and acrylic acid esters (see Figure 8), which would be alternative to the currently present in the industry technologies of obtaining them from non-renewable resources, is the main issue for scientists working in the field of catalysis.

Lactic acid is used in the food industry and for the production of other chemicals and polymers and its production is about 2.7 Mton/year. Lactic acid has three available atoms for adsorption: the oxygen atom of the alcohol group and the two oxygen atoms of the carboxyl group. Based on the literature [75], the lactic acid adsorption over metallic cations gives several possible binding modes at zirconia surfaces: monodentate, bidentate bridging and bidentate chelating, where a dissociative bidentate bridging mode is preferred. The classical pathway through a carbocation proceeds with a very high activation energy. Therefore, the authors suggested another mechanism through a carbanion and succeeded with the acrylic acid formation.

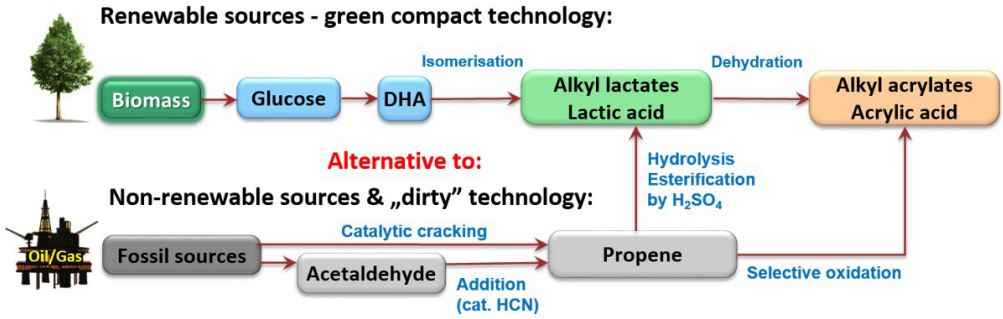

Fig. 8. Scheme illustrating the lactic acid and acrylic acid as well as their esters [44] (DHA=dihydroxyacetone)

From all family of biomass-derived compounds lactic acid is the most promising and can generate multiple final and intermediate chemicals, such as acrylic acid, pyruvic acid, 1,2-propanediol, 2,3-pentanedione or acetaldehyde (see Figure 9) [6, 26]. This compound can also be polymerized into biodegradable plastic, i.e. polylactide (PLA), or solvents.

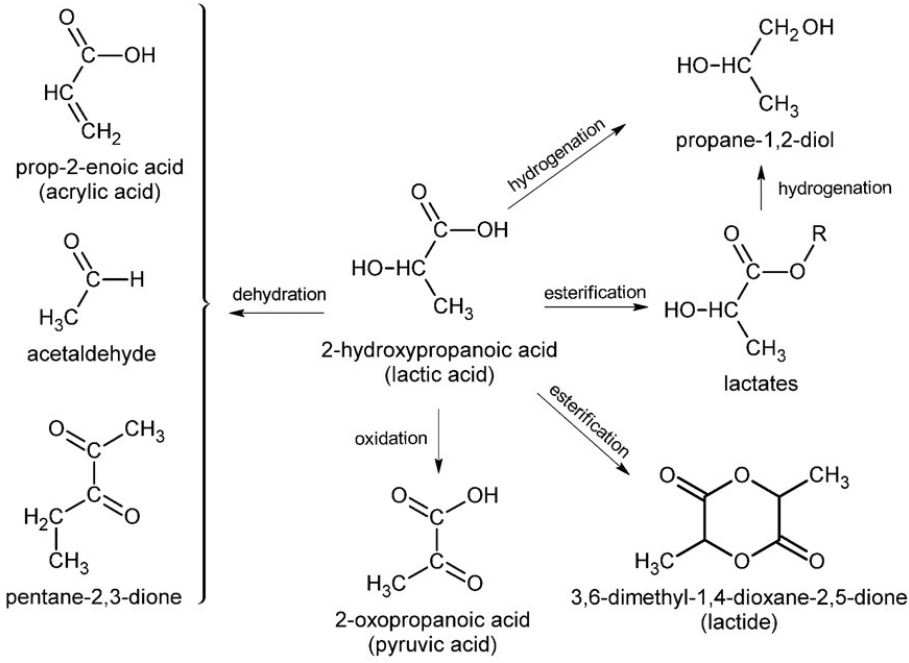

Fig. 9. Scheme illustrating the lactic acid reactions [6]

Dehydration of lactic acid provides the most promising and environmentally friendly way to produce for example acrylic acid. However, the dehydration of lactic acid may be accompanied by other competing reactions, such as hydrogenation, condensation, decarboxylation and esterification, where the decarboxylation to acetaldehyde is one of the

major side reactions and has a large effect on the low selectivity to acrylic acid. To inhibit the formation of acetaldehyde and improve the selectivity of the desired acrylic acid, the effects of many different catalysts are tested.

5. Catalytic dehydration of lactic acid/alkyl lactates to acrylic acid/alkyl acrylates

5.1. State-of-art of actual research of obtaining acrylic acid and alkyl acrylates

Acrylic acid is one of the most important compounds for the synthesis of organic. It is widely used for the preparation of a variety of materials. such as water absorbent polymers, adhesives, textile treating agents (see Figure 10).

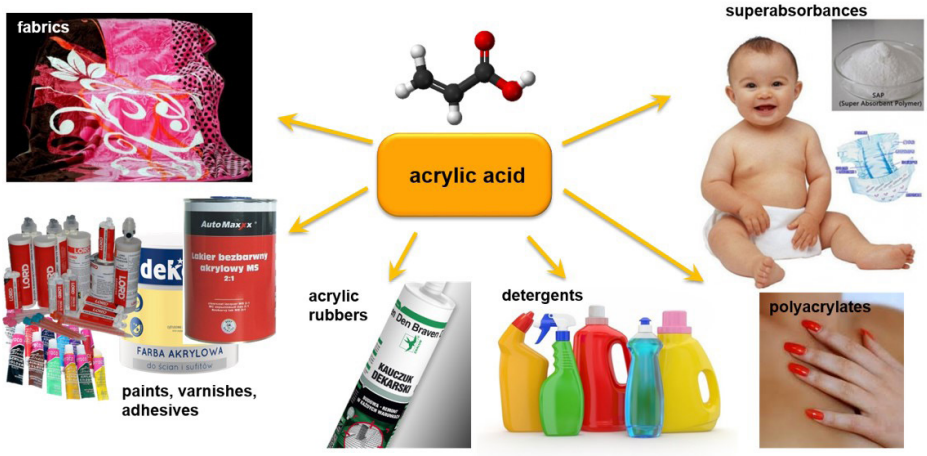

Fig. 10. Scheme illustrating the main directions of acrylic acid processing [76]

The most common industrial process for preparing acrylic acid is the selective oxidation of propylene. This is the basic method of obtaining the product in the fossil industry. Due to the high demand for fossil fuels and the relatively low stocks of crude oil, the price of propylene and its by-products grow, which leads to increased pressure on the production acrylic acid of the propylene.

Acrylic acid is a platform molecule used as a building block to produce acrylate polymers and plastics [77]. Its production had a grown of 4%/year between 2006 and 2011, reaching 4.2Mt in 2011 and was predicted to increase about 5% per year between 2012 and 2017, and recently, its production has been about 4.7 Mton/year. [78]. Acrylic acid is currently produced by the catalytic oxidation of propylene using a two-step process (Figure 2). However, it is widely affected by the propylene price, as it only represents 2% of its global consumption [77]. The value of the acrylic acid market in the 2013 year was equal to 11 billion $ yearly and the forecast value before 2020 is around 18.8 billion $. In the next 5 years, the global demand for acrylic acid will be around 8.169 billion tons/year.

An alternative route of producing acrylic acid is therefore required, especially in the context of the commitment to environment-friendly catalytic processes, for example, a single step dehydration of lactic acid. The catalytic dehydration of lactic acid to acrylic acid has received increasing attention in the last two decades, but high selectivity has proven elusive. Metal-exchanged zeolites are promising catalysts for further development for LA to AA dehydration. However, acrylic acid is rarely obtained selectively from lactic acid because of easy decarbonylation/decarboxylation leading to acetaldehyde and COx. High yields of acrylic acid were obtained using modified zeolites, but they suffered from coking and hydrothermal instability.

In 1958, Holmen was first to show that acrylic acid can be obtained in the dehydration of lactic acid using a mixture of sodium sulfate and calcium sulfate as a catalyst.

One of the methods could be the dehydration of lactic acid over hydroxyapatite (Ca-HAP) catalysts with different mole ratios of Ca/P and calcination temperatures described by Bo Yan *et al.* [79]. Hydroxyapatites (HAP) are known as important acid–based catalysts. According to the study, the HAP sample (with Ca/P = 1.62 and calcination temperature 360 °C) was identified as the most effective for the selective formation of acrylic acid from lactic acid, showing an acrylic acid selectivity within a range of 71–74 % and an acrylic acid yield of 50–62%. The gas-phase dehydration of lactic acid was conducted under atmospheric pressure in a vertical fixed-bed quartz reactor. The reaction feed, an aqueous solution containing 35.7 wt % or 10 mol % lactic acid with space velocity 2.1 h^{-1} and in 360 °C.

Huang *et al.* [80–83] performed the LA dehydration process on NaY zeolites, modified by rare earth metals (lanthanum, cerium, samarium and europium) from which the La-NaY had the best selectivity. The catalysts were obtained by ion exchange of the corresponding cations (lanthanum, cerium, male and europium) in an aqueous nitrate solution. The modified zeolite was marked with the silicon module Si/Al = 4.5. Subsequent scientists have developed a catalyst by modifying NaY zeolite by potassium. The addition of potassium to NaY significantly improved its lifetime [84].

The other method of obtaining an acrylic acid, which was described by Xianghui Zhang *et al.* [85], involves ZSM-5 zeolite as a catalyst. It is well-known that ZSM-5 has strong acidic sites on the surface of H-ZSM-5, which gives a very low selectivity for acrylic acid. Fortunately, the surface acidity of H-ZSM-5 zeolite can be regulated in a wide range through alkaline treatment. At first, the H-ZSM-5 zeolite was treated with the NaOH aqueous solution. The dehydration reaction of lactic acid was carried out in a vertical fixed-bed steel reactor. Studies using 30 wt% lactic acid have shown that for differently modified ZSM-5 catalysts, lactic acid conversion changes little: it is only changing in the small range of 95.8–97.3% in the temperature range of 335–380°C. Although the selectivity for acrylic acid exhibits a volcano-type dependence on NaOH concentrations, the best acrylic acid selectivity with over 65% could be achieved when the concentration of NaOH is 0.3–0.5 mol/L. Increasing the NaOH concentration causes a decreased acrylic acid selectivity and appearance of other unknown products. The best catalytic performance, an achievement of lactic acid conversion of 96.9% and selectivity for acrylic acid accounting to 77.9%, were obtained over the resulted ZSM-5 catalyst treated by 0.5 mol/L NaOH and 0.5 mol/L Na_2HPO_4 under the optimized reaction conditions (350 °C,

LHSV = 4 h^{-1}). One of the main problems is the stability of catalysts for the dehydration reaction of lactic acid. Conversion of lactic acid in a reaction time of 52 hours is still 88% at a selectivity as high as 65% acrylic acid. A slight decrease in conversion and selectivity may be due to the inevitable deposition of coke, which is typical for acid-base catalysts.

Another way to modify ZSM-5 zeolites is by using ion exchange with alkali metals [86]. ZSM-5 zeolite (Si/Al molar ratio = 75) was preheated at 550 °C for 6 h and treated with an aqueous solution of MNO_3 (1 mol/L; M = NH_4, Li, Na, K, Rb, or Cs; 14 g of ZSM-5 zeolite in 140 mL of MNO_3) at 80 °C for 6 h to obtain ion-exchanged ZSM-5. The modified zeolites gave improved catalyst performance in lactic acid dehydration to acrylic acid. The conversion of lactic acid decreases in the following order: H> Li> Na-> K> Rb-> Cs modified ZSM-5. The highest selectivity of acrylic acid was prepared using a catalyst KZSM-5 ($K_{0.84}Na_{0.16}$ZSM-5). These results indicate that the introduction of the alkali metal effectively inhibited the decarbonylation and decarboxylation of lactic acid to acetaldehyde. It has been found that the introduction of alkali-metal cations decreased the total acid-base number, which improved acrylic acid selectivity.

A sequent article by Yan *et al.* discusses the dehydration of lactic acid carried by the Rb+- and Cs+-exchanged Beta zeolite catalysts [87]. In this case, raw powders of as-synthesized Beta zeolite (SiO_2/Al_2O_3 = ca. 40) were used and the Rb+- and Cs+-ions were added by ion-exchange with aqueous solutions of $RbNO_3$ and $CsNO_3$, respectively. The gas-phase dehydration of lactic acid was carried out under atmospheric pressure at 360 °C in a vertical down-flow, fixed-bed tubular quartz reactor. This study shows that the Rb+- and Cs+-exchanged Na zeolites with suitable exchange degrees could be highly efficient for catalyzing the gas-phase dehydration of bio-derivative LA for sustainable AA production. Samples of $Rb_{0.95}Na_{0.05}$ and $Cs_{0.81–0.90}Na_{0.19–0.10}$ were identified as the best performing catalysts for AA production by optimizing the exchange degrees for Rb+ and Cs+, respectively, to uncover the suitable acidity–basicity balance, offering the acrylic acid selectivity as high as 69–70 % and yields higher than 65 mol%.

The alkyl lactates are more promising for acrylic acid and its esters production. Alkyl lactates are easier to vaporize and less polymerizable than lactic acid. Their ester functions that are less reactive limit decarbonylation/decarboxylation reactions. The standard industrial reaction for producing, for example, methyl acrylate is esterification with methanol under acid catalysis (sulfuric acid, p-toluene sulfonic acid, acidic ion exchangers [76]). Ethyl acrylate is produced by acid-catalyzed esterification of acrylic acid, which in turn is produced by oxidation of propylene. It may also be prepared from acetylene, carbon monoxide and ethanol by a Reppe reaction. Biomass as a renewable resource for alkyl acrylate sounds to be more ecologically friendly, and much less robust technology is expected to be developed.

Interest in the use of alkyl lactate instead of lactic acid as a reactant to reach higher acrylic acid selectivity has been previously illustrated for $Ca_3(PO_4)_2$ –$Ca_2(P_2O_7)$ (50/50 wt%) mixture [88]. The highest acrylic acid molar selectivity was found for ethyl lactate (79%), followed by methyl lactate (75%) and lactic acid (54%). Moreover, the use of alkyl lactates could simplify the separation and purification process and reduce production costs [89] even if it would imply the recycling of co-produced alcohols. In that regard, additional molecules of

alkyl lactates could be produced. Alkyl lactates (AL) have been shown to be effective starting materials for the production of acetaldehyde, 2,3-pentanedione, lactide (a biopolymer starting material), and alkyl acrylates (AA) [90]. Growth in the demand for acrylic acid is forecasted at 4.5% per year during 2016-21, driven by the growth of acrylate esters at about 4%. After butyl acrylate and ethyl acrylate, methyl acrylate is the third most important acrylic ester with a worldwide annual production of about 200,000 tons per year [91]. The alkaline earth phosphates have been prepared and evaluated in the gas phase dehydration of ethyl lactate to acrylic acid and ethyl acrylate [92]. However, zeolites are much more promising materials for biomass conversion into lactates and acrylates. Zeolites, microporous and crystalline aluminosilicates, are effective catalysts in many applications [93].

5.2. Nanodesign of zeolites and the process of biomass transformation into acrylic acid

Taking into account all the previously reviewed state-of-art papers concerning biomass valorization into valuable chemicals in our study, we are interested in designing a new theoretical and experimental approach for the synthesis of acrylic acid from lactic acid over zeolite catalysts. The catalyst design of lactic acid dehydration, using both experimental and theoretical methods, helps in further development and synthesis of zeolite with a declared structure and obtaining a structure of substrates, products and intermediates. Actually, in our laboratory, the experimental and theoretical design of zeolite catalysts is performed.

In the theoretical part, the electronic structure of all clusters was calculated by *ab initio* density functional theory (DFT) methods (program StoBe) using the non-local generalized gradient corrected functionals according to Perdew, Burke, and Ernzerhof (RPBE), in order to account for electron exchange and correlation. The stabilization of monomeric and dimeric iron and tin complexes, such as M-OH, HO-M-O-M-OH and M-O-M (where M= Fe, Sn) in the zeolites pore and at the surface (MFI, BEA, FAU) has been investigated. The example is BEA structure (Figure 11), where M-O-M dimers stabilized in micro- and mesopores.

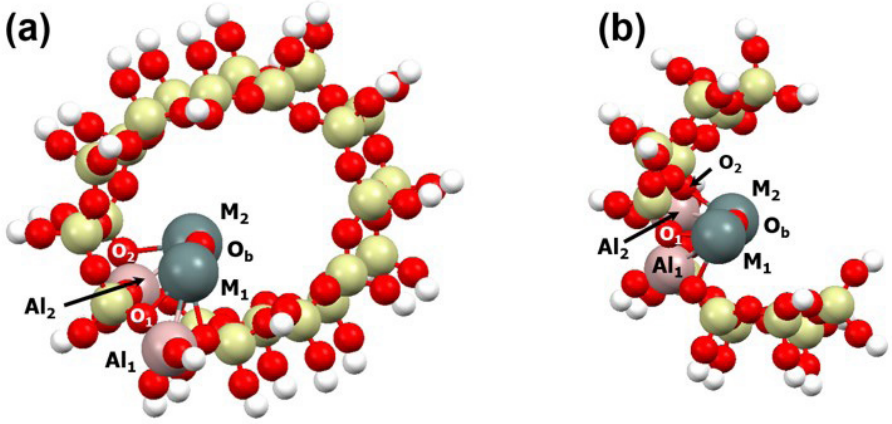

Fig. 11. Dimeric complex M-Ob-M in the BEA: (a) ideal inside pore, (b) after hierarchization

Experimentally, the dehydration reaction of lactic acid was carried out in a vertical fixed-bed quartz reactor (Figure 12) and operated under atmospheric pressure and with a temperature of 350 °C. The reaction feed, which was an aqueous solution containing 40 wt% lactic acid with 2cm^3/h flow rates, was pumped into the reactor and driven by inert gas (50 mL/min).

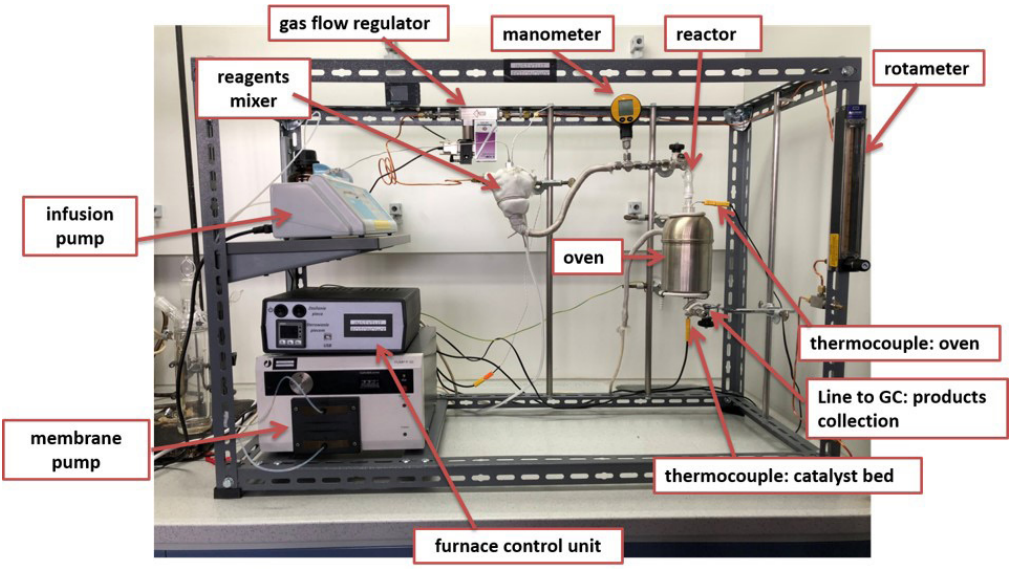

Fig. 12. Unit for catalytic tests in the gaseous phase

The metal M-O_b-M dimers have been found to be stable above oxygen bound with aluminum centers of MFI, BEA and FAU zeolites. The mechanism of direct lactic acid dehydration in Sn- and Fe- zeolites has been found. The geometric compatibility of the metallic dimers and lactic acid allows for the proposed direct dehydration mechanism (see Figure 13), where the oxygen center of the hydroxyl group of LA-a-carbon interacts with the metal center of dimer and hydrogen is subtracted from LA-b-carbon and bound with the bridge oxygen of the metal dimer.

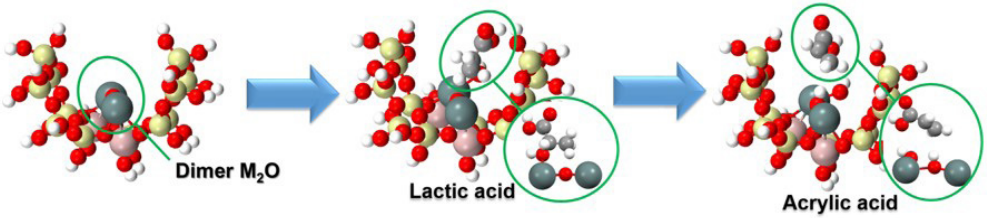

Fig. 13. Dimer M2O, lactic and acrylic acid structures at the surface model of BEA zeolite

The results of our nano-design materials suggest that adsorption of lactic acid is endothermic in the case of Sn-BEA, slightly endothermic in ideal Fe-BEA and exothermic in the case of hierarchical Fe-BEA catalyst. The dehydration of lactic acid into acrylic acid

proceed with an energy barrier. However, the energy level of acrylic acid above Fe-BEA have been found to be lower than the energy level of lactic acid. The hierarchical metal modified BEA zeolite has been found theoretically to be the best catalyst for direct dehydration of lactic acid into acrylic acid. The hierarchization process increases the pore volume as well as increases the chance of adsorption of larger molecules at desired active sites. The theoretical results are confirmed experimentally. Besides acrylic acid, other products have been detected: pyruvic acid, 1,2-propanediol, 2,3-pentanedione, acetaldehyde and lactide. However, the process of lactic acid dehydration is very complex due to the fact of the formation of products in two liquid phases. Therefore, obtaining the full mass balance of reaction is very complicated and required further improvement.

6. Conclusions

The urgent needs for a more sustainable production of chemicals from renewable feedstock (e.g. biomass) have caused intensive research efforts in the search for novel porous nano-materials, such as zeolites. Important properties of zeolites, which make them ideal candidates for the transformation of biomass into high-value chemicals, are their high hydrothermal stabilities. The problematic in using zeolites in biomass conversion is the production of a large number of products. The catalysts are still discovered through a combination of trial-and-error and serendipity due to a limited understanding of the molecular structure and the complexity of active centers. The main goal of the research should be zeolite design in a nano-scale with an improved catalytic performance, optimized for biomass transformation to dedicated chemicals. The research is focused on zeolites with different pore sizes. Another problem is the existence of many phases during processes, e.g. water and organic phases, which makes the process very difficult for industrial scale. Additionally, the products have a tendency to polymerize.

We present here a comprehensive literature study on valuable biomass-derived chemicals and technologies connected with extraction and processing of: aldo-keto isomerization of glucose, 5-hydroxymethylfurfural and furfural, levulinic acid and γ-valerolactone, adipic acid, dihydroxyacetone, lactic acid and acrylic acid. From all the families of such biomass-derived compounds, lactic acid and its alkyl lactates are the most promising and can generate multiple final and intermediate chemicals, such as acrylic acid, alkyl acrylates, pyruvic acid, 1,2-propanediol, 2,3-pentanedione or acetaldehyde. This compound can also be polymerized into biodegradable plastic, i.e. polylactide (PLA), or solvents. Therefore, the development of biomass-derived processes requires a lot of multidisciplinary research before it would be finally applied in industrial practice. However, it is worth considering, especially by using zeolites with a more declare structure and design properties. Therefore, the methodology of designing simultaneously zeolites theoretically and experimentally that we have used gives an exceptional chance to obtain knowledge about the process and simultaneously modify its parameters.

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