Chemocatalysis of sugars to produce lactic acid derivatives on zeolitic imidazolate frameworks

Beatriz Murillo[1], Beatriz Zornoza[1], Oscar de la Iglesia[2], Carlos Téllez[1]*, Joaquín Coronas[1]

[1]Department of Chemical and Environmental Engineering and Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain.

[2]Centro Universitario de la Defensa Zaragoza, Academia General Militar, 50090 Zaragoza, Spain.

*Corresponding author: Dr. Carlos Téllez. Universidad de Zaragoza. c/ Mariano Esquillor s/n. 50018 Zaragoza. Spain. Phone: 34 976 762897. Fax: 34 976 761879. e-mail: ctellez@unizar.es

Abstract

Several research studies related to biorefining have focused on developing routes for biomass conversion into biomaterials or platform molecules. In this work, the ZIFs (zeolitic imidazolate frameworks) ZIF-8 and ZIF-67 have been tested as catalysts in the conversion of sugars (sucrose, glucose and fructose) into methyl lactate. ZIF-8 and ZIF-67 have the same sodalite type zeolite structure but behaved differently in the sugar conversion in methanol due to the respective presence of Zn and Co in their structures. ZIF-8 has been found to be the most active for the conversion of sugars into methyl lactate (yield 42%) and was reused in four catalytic cycles. The chemical and physical effects caused by these cycles on the catalysts have been studied by several techniques (X-ray diffraction, thermogravimetric analyses, infrared spectroscopy, X-ray photoelectron spectroscopy, scanning electronic microscopy and nitrogen adsorption).

Keywords

Biomass, MOF catalysis, Zeolitic imidazolate framework, Sugar conversion, Lactic acid

1. Introduction

There is a growing interest in the development of new technologies based on biomass due to the depletion of fossil fuels and the high energy and chemical consumption worldwide. The concept of biorefining has emerged as an example of the integrated production of fuels (biofuels), heat and electricity (biopower) and biomaterials [1-4]. One of the platform molecules produced from biomass is lactic acid [5], which is the most important hydroxycarboxylic acid due to its wide range of applications in the cosmetics, pharmaceutical and chemical industries [6,7]. Above all, the main use of this compound is in the polymer market, since lactic acid is the precursor for a biodegradable polymer called polylactic acid [8,9] that could substitute polystyrene or polyethylene terephthalate [5].

Over 90 % of commercial lactic acid is produced by a biotechnological route [5], the fermentation of aqueous glucose, but this process has some drawbacks such as a long reaction time because of its low reaction rates, high energy consumption and large amount of waste produced in the neutralization and purification steps [10].

Firstly, homogenous catalysis was studied as an alternative, and various industrial routes from petrochemical resources, such as acetaldehyde, have been used for lactic acid production [11]. Some research studies have reported the use of homogenous catalyst in the production of lactic acid [12,13]. For instance, Zhou et al. [12] developed a method for the conversion of carbohydrates into methyl lactate using $SnCl_4$ as catalyst with inorganic bases. The authors used NaOH to neutralize the protons generated in the methanolysis of $SnCl_4$, increasing the yield to methyl lactate. However, the used catalysts are toxic and corrosive and their recovery is difficult, so this route is not an attractive alternative.

Recent research has focused on heterogeneous catalysis where the catalysts could be recovered and reused with low cost. The challenge is to find an efficient catalyst to produce lactic acid from biomass. Over the past few years, several solid catalysts have been applied for the conversion of sugars. Different zeolites were used for this purpose such as BEA-type zeolite [14-16], MFI-type zeolite [17] and FAU-type zeolite [18,19]. A few mesoporous materials, such as Sn-MCM-41 [17,20-22] and SBA-15 [17] were also studied with good results. In addition, other kinds of solids such as tin-exchanged montmorillonite clay [23], supported noble metal catalysts [24], alumina supported KOH [25] and simple carbon-silica composite [26] were tested in this reaction.

Catalytic lactic acid production using sugars has a complex mechanism (see reaction pathway in Fig. S1) where several stages are involved. Lewis acid sites play an essential role in retro-aldol reaction, isomerization and 1,2-hydride shift; and Brønsted acidity is important in hydrolysis and dehydration [27]. It should be pointed out that direct obtaining of methyl lactate has some advantages in front of lactic acid, due to the fact than an esterification step and a hydrolysis stage are need for lactic acid purification [5]. Besides methyl lactate is a lactic acid precursor, it has its own applications such as green solvent.

Metal-organic frameworks (MOFs) are crystalline hybrid compounds formed by a metal cluster coordinated with organic linkers. These materials present a high porosity and an easy tunability of their pore size and shape and final functionality [28-31]. For these reasons, MOFs are considered as potential materials in several applications such as adsorption [32], gas separation and storage [33], membranes [34] and medicine [35]. However, the most promising application of this family of materials is perhaps catalysis [36-42].

Within the context of MOFs, ZIFs (zeolitic imidazolate frameworks) are a subclass with zeolite-type topology [43]. ZIFs are well-known due to their high chemical and thermal stability, the ease of obtaining them, their high porosity and their 3D porous and isotropic framework. Therefore, this class of compounds is very promising for a wide range of applications. ZIF-8 and ZIF-67, whose metal atoms are Zn and Co, respectively, both have sodalite type zeolitic topology [44,45]. Crystal structures of both solids are represented in Fig. 1. In ZIF-8, ZnN_4 tetrahedra are linked by methylimidazolate ligands forming a 3D framework with large cavities of 11.6 Å accessible by small windows of 3.4 Å. On the other hand, the ZIF-67 framework, where CoN_4 tetrahedra are connected by imidazolate linkers, presents cavities of 11.4 Å and small windows of 3.3 Å [45]. Note that even though the pore apertures of the ZIFs are small, their flexibility induced by the organic linkers plays an important role. The microporous catalysts studied here have cavities large enough to accommodate the molecular diameters of glucose and fructose (ca. 8.5 Å) [46], as also occurred when encapsulating caffeine (6.1 x 7.6 Å) in ZIF-8 [47]. In addition, the so-called gate opening effect was also explained for ZIF-7 [48] when adsorbed guest species with size larger than that of the MOF aperture.

Given the characteristics of the ZIF-8 material, it is one of the most extensively studied ZIFs and has been tested as a heterogeneous catalyst for a number of reactions including the Knoevenagel reaction [49], transesterification [50], Friedel-Crafts acylation [51], monoglyceride synthesis [52], the formation of carbonates [53], hydrogen production [54] and multifunctional catalyst [55]. ZIF-67 has also been studied as a heterogeneous catalyst, with better performance in the formation of carbonates than ZIF-8 [56].

There are few publications concerning MOFs used as catalysts in biomass transformation. Cirujano et al. have recently reported the use of Zr-containing MOFs (UiO-66 and UiO-66-NH_2) for the esterification of levulinic acid with some alcohols, obtaining high alkyl levulinates yields [57]. Other authors have functionalized MOFs for fructose conversion [58,59] and glucose isomerization [60].

Given that the use of solid acid catalysts for the conversion of sugars has become attractive for many researchers and there remains the challenge of finding new applications of MOFs, in this work we report on the use of ZIF-8 and ZIF-67 as catalysts in the transformation of sugars in methanol (sucrose, glucose and fructose) to methyl lactate. Both ZIFs could be interesting alternative materials in catalytic biorefinery for this new kind of processes.

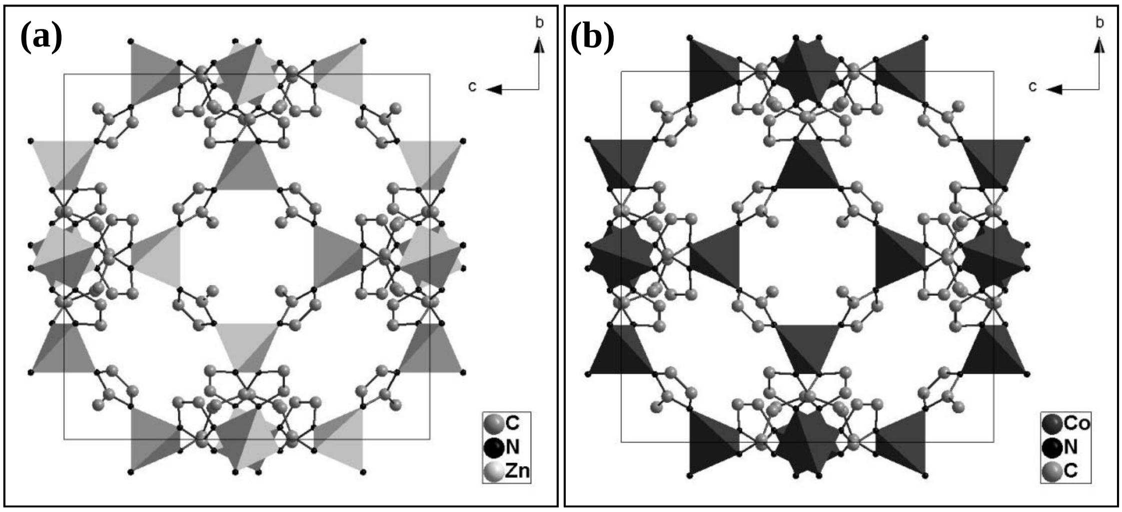

Fig. 1. Representation of ZIF-8 (a) and ZIF-67 (b) frameworks using Diamond 3.2 software. Crystal data from CCDC (The Cambridge Crystallographic Data Centre): ZIF-8 (CCDC code VELVOY)[44]; ZIF-67 (CCDC code GITTOT)[45].

2. Experimental

2.1. Catalyst preparation

ZIF-8 was synthesized using a previous method reported elsewhere [47]. The precursor solution had a molar ratio of Zn^{2+}:2-methylimidazole:H_2O:MeOH = 1:12:313:177. This solution was prepared as follows. Firstly, 3.15 g of 2-methylimidazole (99 % purity, Sigma-Aldrich) was dissolved in 20 mL of methanol (Multisolvent HPLC grade, Scharlau). Secondly, 0.95 g of $Zn(NO_3)_2 \cdot 6H_2O$ (98 % grade, Sigma-Aldrich) was dissolved in 20 mL of methanol and 10 mL of deionized water. Each solution was stirred individually for 10 min after which the solution containing the metal was added to the linker solution. The mixture was maintained at room temperature under stirring for 2 h. Then the solution was centrifuged at 10,000 rpm for 20 min. The solid product was washed with methanol twice and dried at 70 ºC overnight.

The preparation method of ZIF-67 was the same, but changing the metal by using Co instead of Zn. In both cases, the same number of moles of metal was employed, so the molar ratio of the precursor solution was Co^{2+}:2-methylimidazole:H_2O:MeOH = 1:12:313:177. In this case, 0.93 g of $Co(NO_3)_2 \cdot 6H_2O$ (98 % grade, Sigma Aldrich) was used as the cobalt source.

2.2. Catalytic reaction

The sugar conversion to methyl lactate was carried out in a batch reactor, a 35 mL Teflon-lined stainless steel autoclave. Glucose (99 %, Alfa-Aesar), fructose (99 %, Alfa-Aesar) and sucrose (99 %, Fluka) were chosen as representative carbohydrates due to their low cost, simplicity and abundance.

The reaction was performed by dissolving 225 mg of carbohydrate in 8.0 g of methanol (Multisolvent HPLC grade, Scharlau). Besides, 30 mg of naphthalene (99 %, Sigma-Aldrich) was added as internal standard for subsequent quantification of the yields. The amount of catalyst added varied from 80 to 500 mg, but a normal batch was loaded with 160 mg of catalyst. The mixture with the sugar totally dissolved was transferred to a 45 mL Teflon-lined autoclave and the synthesis was carried out in an oven. The oven was heated in a ramp of 1 h up to the desired reaction temperature, varied from 80 to 160 ºC. The reaction time starts when the reaction temperature is reached and it was varied between 1 and 48 h under rotating conditions (15 r.p.m, i.e. the whole autoclave rotates perpendicularly to its axial axis) (see in Fig. S2 the rotation inside the oven). 15 r.p.m. was chosen as rotation speed in the oven because it has been observed with ZIF-8 as catalyst that there were no apparent mass transfer limitations in the production of methyl lactate (i.e. no product yield increase, see Fig. S3).

Afterwards, the catalyst was recovered by centrifugation and the reaction liquid was analyzed by gas chromatography with a mass detector (GC-MS). The equipment was an Agilent 6850 GC system with a capillary column HP-5MS (30 m x 0.250 mm x 0.25 μm) coupled with an Agilent 5975 MSD. The yields of the different products were calculated using the internal standard method and calibration curves using commercial compounds: methyl-S-(-)-lactate (98 %, Sigma-Aldrich), methylglyoxal 1,1-dimethylacetal (97 %, Sigma-Aldrich), also called pyruvaldehyde dimethyl acetal, and 1,1,2,2–tetramethoxypropane (99 %, Sigma-Aldrich).

The determination of sugars was carried out using a commercial analytical method (Sucrose/Fructose/D-Glucose Assay Kit, Megazyme). The analysis was carried out as follows: firstly, the sugars samples were mixed with a solution which contains enzymes (different for each sugar), these enzymes transform sugars to glucose-6-

phosphate (G-6-P), and reaction lasts for a few minutes. Then another solution containing nicotinamide-adenine dinucleotide phosphate (NADP+) and enzyme glucose-6-phosphate dehydrogenase (G6P-DH) was added. In the presence of this enzyme, G-6-P is oxidized by NADP+ producing its reduced form (NADPH), which is measured by increasing its absorbance at 340 nm using a UV-spectroscopy (V-670 Jasco UV−vis spectrophotometer).

A series of experiments was carried out using sucrose as substrate with reused ZIF-8. The reaction conditions were 160 ºC for 24 h with 160 mg of catalyst. Between each run, the recovered solid was dried under vacuum at 190 ºC for 12 h, in order to remove adsorbed compounds.

2.3. Catalyst characterization

The diffraction patterns of the samples were measured by X-ray diffraction (XRD) using a D-Max Rigaku X-ray diffractometer with Cu-Kα_1 radiation (λ = 1.5418) and a graphite monochromator. Thermogravimetric analyses (TGA) were carried out using Mettler Toledo TGA/SDTA 851e equipment. Samples were heated in air up to 850 ºC with a heating rate of 10 ºC/min. Scanning electronic microscopy (SEM) images were obtained over Pt-coated specimens using an Inspect F50 model scanning electron microscope (FEI). Nitrogen adsorption-desorption isotherms were obtained with a Micromeritics Tristar 3000. Previously, the samples were degassed at 190ºC for 8 h under vacuum. Fourier transformed infrared spectra were measured on a Bruker Vertex 70 FTIR with a deuterated triglycine sulfate (DTGS) detector and ATR Golden Gate accessory in the range 600-1,800 cm^{-1}, with an accuracy of 4 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed with an Axis Ultra DLD (Kratos Tech.). The spectra were excited by a monochromatized Al Kα source (1,486.6 eV) at 15 kV and 10 mA and a pass energy of 20 eV was used for the individual peak regions. Binding energies were referenced to the internal standard C 1s (284.5 eV).

3. Results and discussion

3.1. Catalyst characterization

The catalysts were characterized by different techniques in order to check their properties and stability. Fig. 2a shows a comparison of the experimental XRD patterns of as-synthesized materials (ZIF-8 and ZIF-67) with those simulated from their single crystal structures. There is a high degree of correspondence between the simulated and experimental patterns and they are in good agreement with those previously reported [44,45]. Both materials have the same crystalline framework corresponding to the sodalite structure and therefore their XRD patterns are similar. The wider peaks of ZIF-8 are consistent with a smaller particle size, as will be shown below.

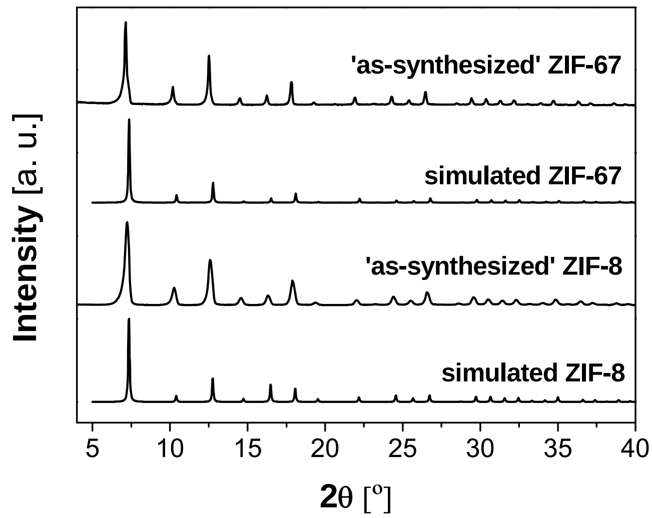

Fig. 2. XRD patterns of simulated ZIF-8, 'as-synthesized' ZIF-8, simulated ZIF-67 and 'as-synthesized' ZIF-67. Simulated XRD patterns are obtained from crystal structure data from CCDC.

Thermogravimetric analyses (see Fig. 2S4) of the catalysts made in air show that ZIF-8 was thermally stable up to 450 ºC, but ZIF-67 only up to 400 ºC. This may be due to a stronger catalytic degradation in air of the metal Co present in ZIF-67, compared with the Zn in ZIF-8.

The size and morphology of the catalysts were studied by SEM. In Fig. 3a, ZIF-8 crystals are observed with a rhombic dodecahedron shape and a 100-150 nm size, while Fig. 3b shows crystals of ZIF-67 with the same well-defined shape of around 1 µm size. The growth kinetics of ZIF-67 are faster than ZIF-8, so bigger crystals are formed, according to a previous report [61].

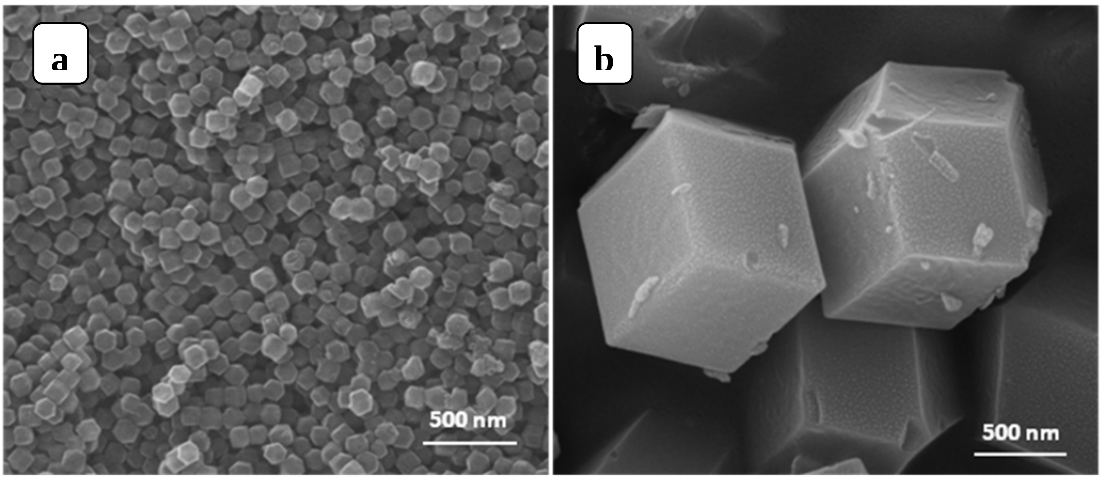

Fig. 3. SEM images of ZIF-8 (a) and ZIF-67 (b).

The textural properties, such as BET specific surface area and pore volume, of ZIF-8 and ZIF-67 were measured. The BET specific surface area is slightly larger for ZIF-67 (1,450 $m^2 g^{-1}$) than for ZIF-8 (1,391 $m^2 g^{-1}$). The same trend in pore volume is observed, 0.69 $cm^3 g^{-1}$ for ZIF-67 and 0.66 $cm^3 g^{-1}$ for ZIF-8. The similar textural properties for both materials are in agreement with their similar ZIF topology and with the similar cell volumes of 4,905.2 $Å^3$(ZIF-8) [44] and 4,877.5 $Å^3$ (ZIF-67) [45].

3.2. Catalytic tests

The zeolitic-imidazolate frameworks (ZIFs) ZIF-8 and ZIF-67 were tested as solid catalyst in the transformation of hexoses (glucose, fructose) and sucrose into methyl lactate in a methanol medium. The results of the sugar conversion with all these catalysts are summarized in Table 1. Other MOF based catalysts (HKUST-1 (Cu), MIL-53(Al) and MIL-101(Cr)) with good initial expectations gave rise to methyl lactate yields below 5 %, thus they were discarded from the in-depth study.

Table 1. Catalytic results obtained for sugar conversion with different catalysts. Showing yields to methyl lactate (ML), pyruvaldehyde dimethyl acetal (PADA), 1,1,2,2-tetramethoxypropane (TMP) and non-identified products (n.i.p.). Error of these values are shown in Table S1.

Entry	**Catalyst**	**Substrate**	**T^a** (ºC)	**Yields** (%)				**Total yield** (%)	**Sugar conversion** (%)
				ML	PADA	TMP	n.i.p.		
1	Blank	Sucrose	160	1.4	2.5	0.1	4.3	8.3	88.6
2	Blank	Glucose	160	1.1	2.5	-	6.0	9.6	87.3
3	$Zn(NO_3)_2\cdot 6H_2O$ [a]	Sucrose	160	22.1	1.4	0.6	3.5	27.6	98.7
4	$Zn(NO_3)_2\cdot 6H_2O$ [a]	Glucose	160	19.6	2.4	0.3	2.5	24.8	94.5
5	$Co(NO_3)_2\cdot 6H_2O$ [a]	Sucrose	160	25.9	0.2	0.1	1.2	27.4	> 99.1
6	$Co(NO_3)_2\cdot 6H_2O$ [a]	Glucose	160	23.0	-	-	1.2	24.2	98.5
7	ZIF-8	Sucrose	160	34.8	1.9	0.4	3.3	40.4	> 99.1
8	ZIF-8 [a]	Glucose	160	19.8	0.8	0.1	2.0	22.7	98.1
9	ZIF-8 [a]	Fructose	160	10.5	-	-	1.5	12.0	97.9
10	ZIF-67	Sucrose	160	19.1	0.1	0.1	2.4	21.7	65.9
11	ZIF-67	Glucose	160	10.4	0.2	0.1	2.0	12.7	78.5
12	ZIF-8	Sucrose	120	6.1	0.1	0.2	9.1	15.5	75.4
13	ZIF-8	Sucrose	80	2.2	-	-	7.2	9.4	74.9

Reaction conditions: 24 h, 160 mg of catalyst and 225 mg of sugar. [a] Reaction time: 20 h.

First of all, blank experiments without catalysts were carried out. Although high conversions of sugar were obtained in these experiments, methyl lactate (ML) was detected in small quantity, giving rise to 1.4 ± 0.9 % and 1.1 ± 0.7 % (error derived from 3 different experiments) for sucrose and glucose, respectively (Entries 1, 2; Table 1). Nevertheless, Holm et al. found that sucrose and glucose gave methyl lactate yields with no catalyst of 6 % and 5 %, respectively [14].

Experiments with $Zn(NO_3)_2{\cdot}6H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ were carried out in order to compare the performance of the metal salts with those of the corresponding ZIFs (Entries 3 – 6; Table 1). In these experiments, the same conditions and amount of metal as for the corresponding ZIF were used. ZIF-8 shows better results than its precursor metal salt. About 10 % more yield of methyl lactate was achieved with sucrose as substrate, 22.1 % with the salt and 34.8 % for the solid catalyst ZIF-8. Thus, the best performance of the heterogeneous catalysis is obvious and it will be of interest to study this MOF as catalyst in the conversion of sugars in greater depth. In contrast, the ZIF-67 catalyst did not improve on the results of the corresponding Co salt.

The sugar (sucrose, glucose) conversion using Co and Zn salt are similar. However, comparing the performance of ZIF-8 and ZIF-67 (Entries 7 – 11; Table 1), it can be seen that the methyl lactate yield obtained from sucrose at 160 ºC in 24 h using ZIF-67 as catalyst was only 19.1 %. Nevertheless, the methyl lactate yield reached 34.8% with ZIF-8, in the same reaction conditions. Although both solids had the same sodalite structure (see Fig. 1), in this reaction ZIF-67 showed lower catalytic activity than ZIF-8. There are two factors that can explain this behavior: the crystal size and the acidity of the metal sites. Firstly, the crystal size of ZIF-67 is larger (about 1 μm) than that of ZIF-8 (100-150 nm); thus, in smaller crystals the accessibility of reactants to the active sites is improved (see Fig. 3). Secondly, Lewis acid sites are needed for carrying out the conversion of sugars to methyl lactate [14] and its presence determined by pyridine adsorption has been reported in the literature in ZIF-8 [62]. In fact, ZIF-8 has stronger acid sites while the catalytic sites of ZIF-67 are moderately acid, according to measurements in the literature using NH_3 and CO_2 temperature-programmed desorption [57].

Some by-products were detected by GC-MS such as pyruvaldehyde dimethyl acetal (PADA), 1,1,2,2-tetramethoxypropane (TMP) and others which were not identified. Their yields are also shown in Table 1. However, the yields to these by-products were quite low, so the catalysts presented high yield towards methyl lactate.

In the case of the catalyst ZIF-8, the sucrose reaction was studied at 80, 120 and 160 ºC (Entries 7, 12, 13; Table 1), finding 160 ºC as the best temperature from the point of view of the yield to methyl lactate. Temperatures of 80 and 120 ºC were found to be too low for the transformation of sucrose into methyl lactate, showing yields below 10 % (Entries 12, 13; Table 1). In addition, sucrose conversions at 80 and 120 ºC were about 75 %, while at 160 ºC it was near 100%. A high reaction temperature was likely to be favorable not only for a complete reaction, but also for yield towards methyl lactate.

Fig. 4 shows the performance of the catalyst ZIF-8 with different sugars (sucrose, glucose and fructose) as a function of reaction time. At short times (1 h), glucose and fructose (initial reaction rates 191 and 143 g ML (g catalyst·h)$^{-1}$, respectively) are more reactive and gave a higher ML yield than sucrose (initial reaction rates 75 g ML (g catalyst·h)$^{-1}$). At longer times, sucrose as substrate gave the highest methyl lactate yield. Ca. 35.0 % of methyl lactate yield was reached at 24 h using sucrose, increasing only up to 36.4 % after 48 h. This may be due to the thermostability and hydrolytic resistance of the disaccharide and the slow release of hexoses from sucrose in solution which prevents unwanted side reactions with the more reactive glucose and fructose [27]. As a consequence in contrast to sucrose, the hexoses had the best performance at 12 h of reaction, reaching methyl lactate yields of 18.1 % and 20.9 % from fructose and glucose, respectively. Using ZIF-67 as catalyst (Table 1) after 20 h of reaction, the methyl lactate yield was bigger for sucrose than for glucose, similar to when the ZIF-8 is used as a catalyst.

It is worth mentioning that the carbon balance, taking into account all the products detected and the sugar conversion, did not reach 100 %. This was probably caused by the production of some polymerization products, humic acids o other carbonaceous compounds which were not detected by gas chromatography. This kind of compounds of unwanted reactions is, certainly, formed in greater amounts in glucose and fructose that sucrose and at longer times it may be responsible to react with methyl lactate reducing their yield.

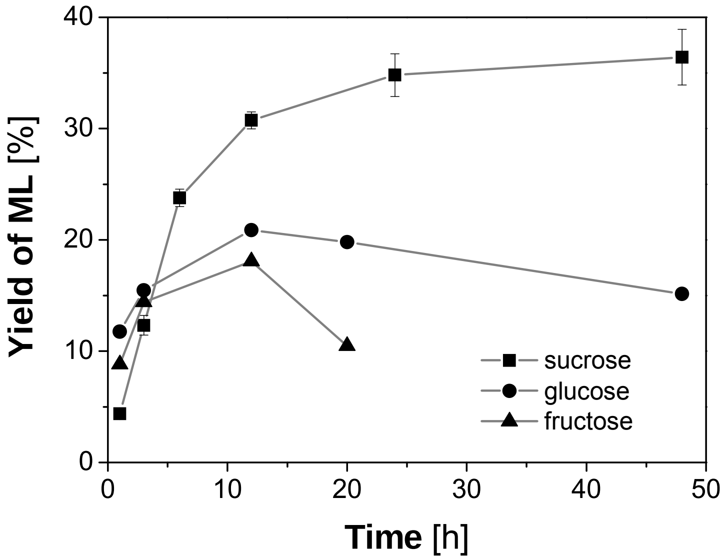

Fig. 4. Yield of methyl lactate (ML) obtained over ZIF-8 using different sugars as reactants. Error bars in the case of sucrose derived from at least 4 different experiments (Reaction conditions: 160 ºC, 160 mg of catalyst and 225 mg of sugar). Profiles of concentration of ML and other products are shown in Fig. S5.

The influence of the amount of catalyst present in the reaction mixture was also studied (80-500 mg) and the results are presented in Fig. 5. The tests were carried out at 160 ºC for 24 h and sucrose was used as the carbohydrate feedstock. 160 mg can be considered as the optimum value (methyl lactate yield ~35%), since with lower amounts of catalyst only a 20 % methyl lactate yield was barely reached, while with double (methyl lactate yield ~37%) or even with triple (methyl lactate yield ~42%) the amount of catalyst the increase in the methyl lactate yield was less significant.

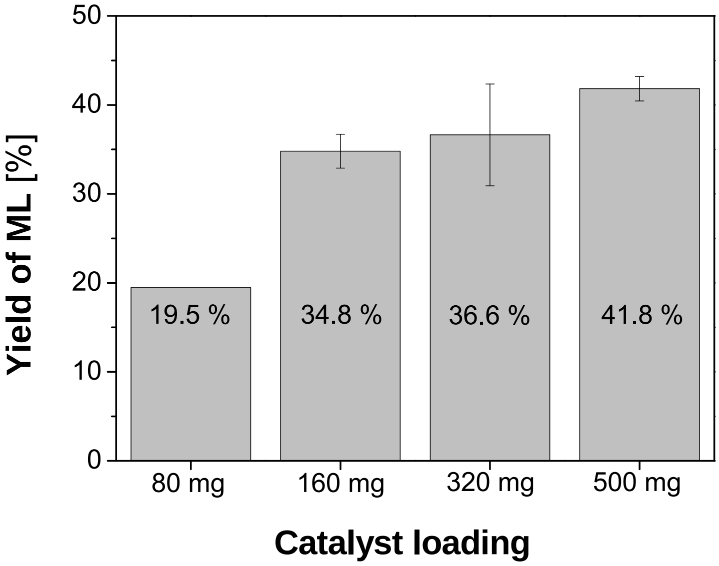

Fig. 5. Comparison of different amounts of ZIF-8 in the conversion of sucrose into methyl lactate (ML).Error bars derived from at least 3 different experiments. (Reaction conditions: 160 ºC,24 h and 225 mg of sugar).

In a previous work, we proposed a possible reaction pathway for the transformation of glucose in the same conditions, but with silicate (MCM-41, JDF-L1, AM-4, UZAR-S1, UZAR-S2) based catalysts, which may be applicable to this case [21]. Different reactions take place in the conversion of sugars to methyl lactate (see Fig. S1). The first step when using polysaccharides corresponds to their hydrolysis, producing sugars with less carbon content. In consequence, sucrose hydrolyzes forming glucose and fructose. Afterwards, the isomerization of glucose to fructose or vice versa occurs. Then the retro-aldol reaction of fructose gives rise to trioses, i.e. DHA (dihydroxyacetone) or GLY (glyceryaldehyde), together with an isomerization step. The next steps involve the dehydration of the trioses, although there is no agreement as to whether DHA (ketose form) or GLY (aldose form) is the final dehydrate intermediate. It is thought that the reaction to methyl lactate could start from either of these precursors.

The dehydration reaction produces pyruvic aldehyde which is prone to a nucleophilic attack on its aldehyde carbonyl with an alcohol (methanol in this case), and the corresponding hemiacetal is formed. The last step is a 1,2-hydride shift, either the incorporation of another methanol molecule forming the pyruvaldehyde dimethyl acetal (PADA) or the isomerization into methyl lactate. The alkyl acetal can react with another methanol molecule and form 1,1,2,2-tetramethoxypropane (TMP).

It has been reported that Lewis acid sites play an important role in both isomerization steps and the 1,2-hydride shift. Besides, it should be noted that the retro-aldol step occurred from fructose; however, the same reaction could occur from glucose and generate some polymer architectures [5].

3.3. Reuse of ZIF-8

Given the high methyl lactate yield (35 %, Table 1), the reusability tests of ZIF-8 were carried out using sucrose as substrate at 160 ºC for 24 h with 160 mg of catalyst in each run. The performance of this catalyst in consecutive catalytic cycles was compared with that of Zn salt used in the synthesis of ZIF-8. For making the comparison as real as possible, the amount of salt used corresponded to the moles of Zn contained in 160 mg of ZIF-8 (Fig. 6). An activation step between runs was carried out because a thermogravimetric analysis (Fig. 7) showed that some compounds remained adsorbed (weight loss between 165 and 300 ° C) on the recovered ZIF-8 after the reaction process. The activation consisted of drying the recovered solid under vacuum at 190 ºC for 12 h, being enough to remove the adsorbed compounds related to mentioned weight loss (see activated recovered solid in Fig. 7). It should be noted that after the first catalytic cycle for sucrose, that means in the second catalytic cycle, without activation the ML yield was 23.8%, while if the catalyst was activated the ML yield increased up to 29.1%. Other alternatives for activation were studied, such as methanol washing and calcination at different temperatures, but none of them was as successful as vacuum drying either because the adsorbed compounds were not removed or because the ZIF-8 structure was lost.

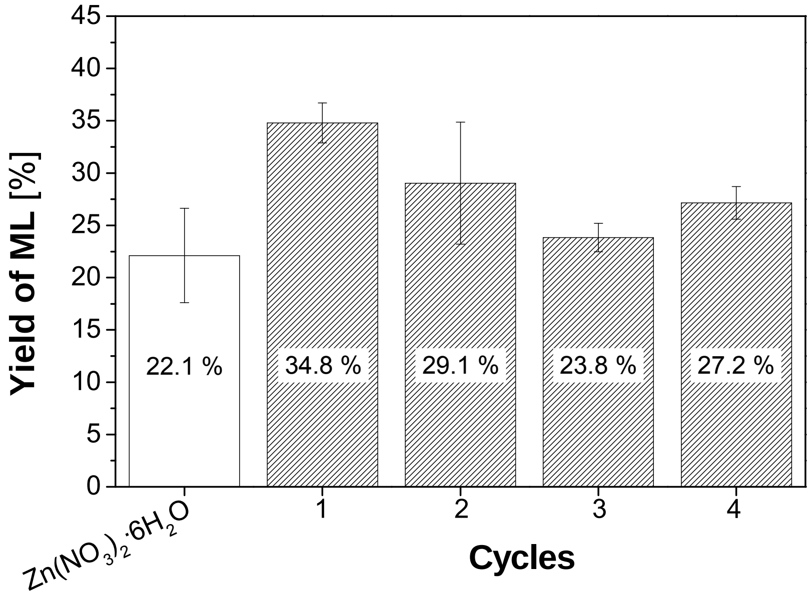

Fig. 6. Reusability of ZIF-8 for the conversion of sucrose to methyl lactate (ML). (Reaction conditions: 160 ºC, 24 h, 160 mg of catalyst and 225 mg of sugar.

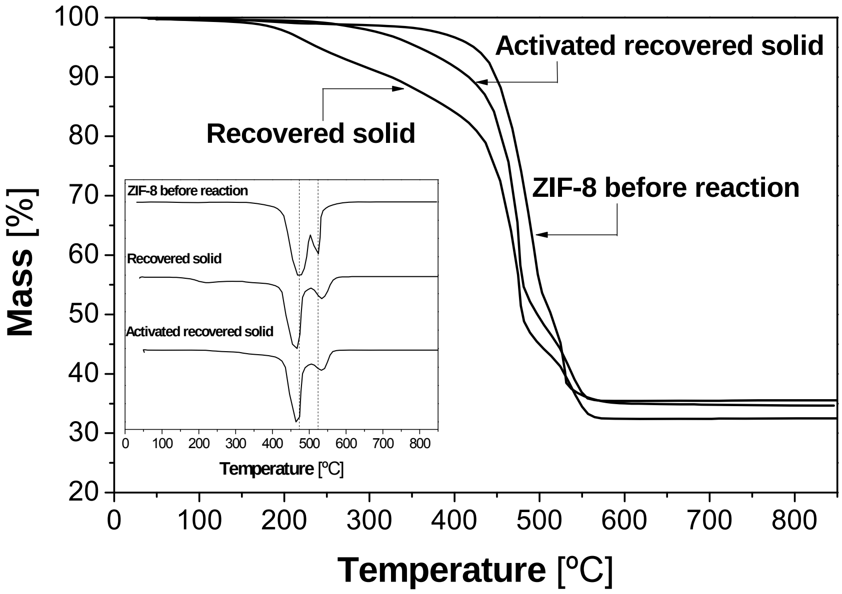

Fig. 7. TGA curves of catalysts: ZIF-8 before reaction, recovered solid after reaction and activated recovered solid by drying under vacuum. The inset shows the corresponding derivatives.

Characterization by ATR spectroscopy was used as a complement to the thermogravimetric analysis and to identify the nature of the adsorbed compounds. Fig. 8a depicts an IR peak at 1090 cm^{-1}which indicated the presence of a C-C bond in the recovered solid that did not exist in fresh ZIF-8. This suggests that some carbonaceous species were adsorbed in the catalyst after reaction. By means of activation this peak disappeared, which confirmed that most of the compounds were successfully removed.

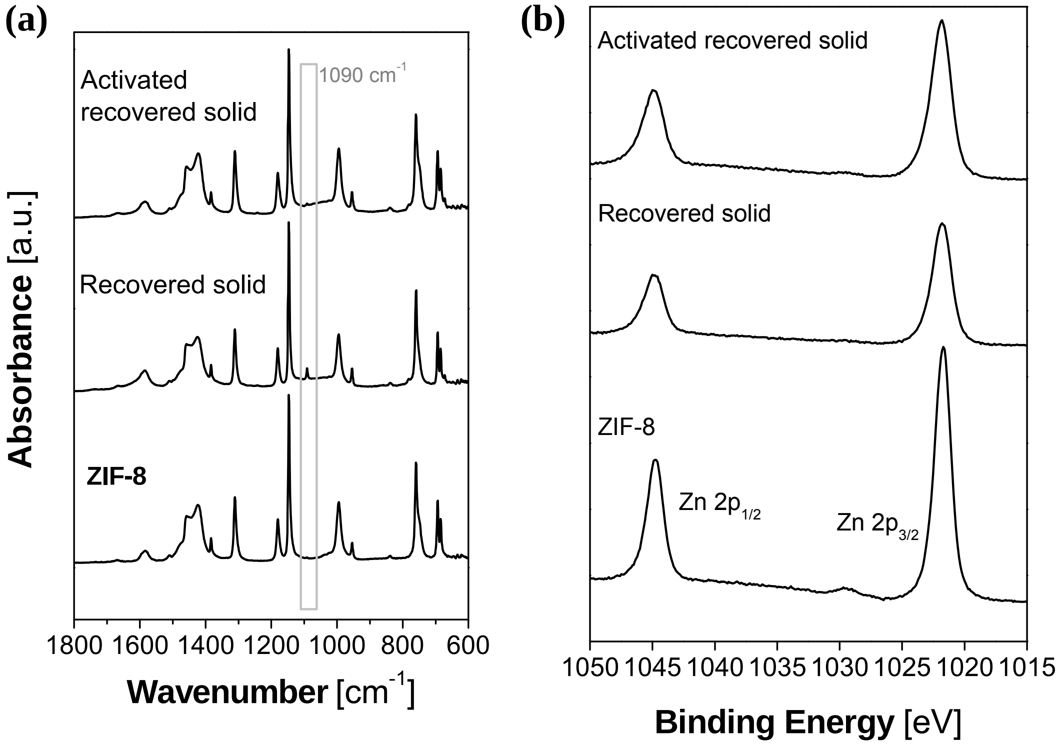

Fig. 8. ZIF-8 before reaction, recovered solid after reaction and activated recovered solid by drying under vacuum: (a) ATR spectra. (b) Zn 2p XPS spectra.

More information about the chemical structure of the recovered solid was achieved by XPS spectroscopy. The corresponding spectrum was compared with that of fresh ZIF-8. Binding energy related to Zn 2p (1021.7 eV) did not change for the two samples (see Fig. 8b) although there was a decrease in the intensity and peak broadening which is related to loss of crystallinity, as observed by XRD. The Zn 2p XPS shows the peak FHWM broadens post-reaction, indicative of the formation of a range of chemical environments in the spent catalyst. This deactivation is further evidenced by the change in N/Zn surface composition given in Table 2. Regarding the N/Zn ratio, fresh ZIF-8 was almost at the theoretical value, i.e. 4.0 corresponding to ZnN_4 tetrahedra in the ZIF-8 framework. After the catalytic reaction, the reduction of N/Zn at the surface was significant (2.0) and could be related to some ligand degradation. The C/N atomic relation increased, related to the above-mentioned adsorbed compounds. Finally, the C/N ratio decreased upon reactivation, consistent with the cleaning of the catalyst surface.

Table 2. XPS results, atomic relation between elements for ZIF-8 before reaction, recovered solid after reaction and activated recovered solid by drying under vacuum.

Sample	C/N	N/Zn
ZIF-8	2.3	3.9
Recovered solid	4.6	2.0
Activated recovered solid	3.5	2.6

The ZIF-8 catalyst could be reused for at least 4 cycles with a loss of activity from 34.8 % to 27.2 %, as shown in Fig. 6. The methyl lactate yield in the first run was over 35 %, while in the subsequent runs it decreased to about 25 %.This decrease is consistent with the adsorption of some compounds which could not be removed during the reaction itself. The degradation of the ZIF-8 structure, probably more intense at the particle surface, cannot be discarded since the textural properties of the catalyst were also affected (see Table 3).

Other characterization techniques were applied to the catalysts after the catalytic runs. There was no difference in terms of XRD patterns in the ZIF-8 before reaction and after the catalytic cycles, as can be observed in Fig. 9. This confirms that the structure in bulk is maintained during the catalytic tests. However, the intensity of the first peak (around 7.2º) decreased as the number of runs increased (from about 47,000 to 20,000 counts for the fresh and fourth cycle catalysts, respectively). In Fig. 9 the percentage of crystallinity is presented, it was calculated respect to the peak at $2\cdot\theta$=7.2º, the catalyst before reaction corresponding to 100%. Therefore, a reduction in crystallinity is more than evident, in agreement with the previous XPS characterization which suggested some surface changes.

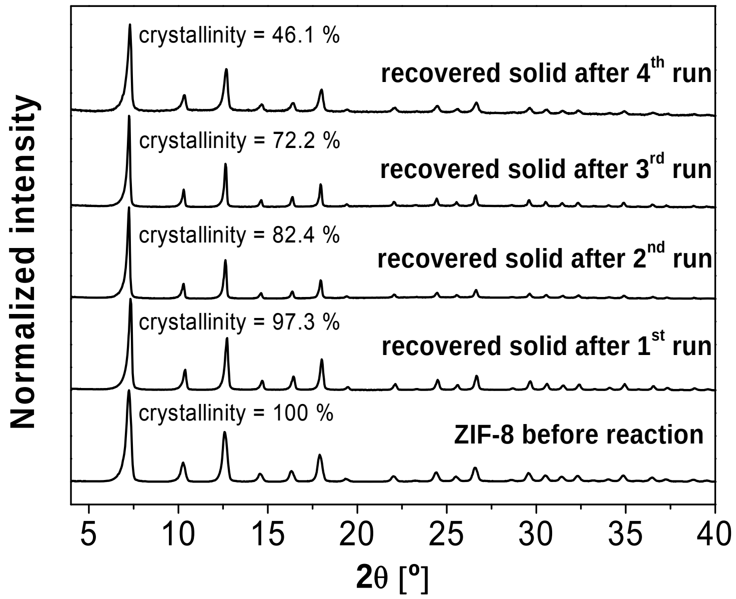

Fig. 9. XRD patterns of ZIF-8 before the reaction (fresh catalyst) and recovered solids after the various catalytic cycles. Including percentage of crystallinity, referred to catalyst before reaction.

After each reaction cycle, it was measured N/Zn and C/Zn atomic ratios by EDX (Table S2) in activated recovered solid. By increasing the number of reaction cycles, there is a decrease of the N/Zn atomic ratio which would agree with the loss of crystallinity and the C/Zn ratio decreases slightly indicating that Zn scarcely leaches.

Table 3 summarizes the textural properties of fresh ZIF-8 and used ZIF-8 after four successive catalytic runs. The BET specific surface area was reduced after each cycle from the initial value of 1,391 to 757 m^2 g^{-1} after the fourth run. A parallel decrease in pore volume also occurred throughout the cycles (from 0.66 to 0.48 $cm^3 \cdot g^{-1}$). These changes are in line with the previous TGA, FTIR and XPS results, suggesting the adsorption of some compounds on the MOF surface. Besides, some structure collapse from the particle surface to its interior could be possible, even though the XRD patterns always correspond to the sodalite type structure of ZIF-8 (Fig. 9). SEM images for activated recovered solid after the first and second reaction cycles (Fig. S6) do not show apparent changes in the morphology, but the edges are rounded after the third reaction cycle (Fig. S6). After the fourth reaction cycle, Fig. 10 shows how the ZIF-8 crystals exhibited some hollow particles, even though the typical rhombic dodecahedron shape was maintained. These hollows suggest dissolution which may contribute, together with the above-mentioned adsorption on the catalyst surface, to the loss of activity at least up to the third cycle (see the methyl lactate yield in Fig. 6). However, the increase in activity from the third to the fourth cycle could be due to these hollows allowing better access to the active sites.

Table 3. Textural properties of the catalyst after reaction cycles. (BET specific surface area and pore volume measured at P/P^o = 0.97 by nitrogen adsorption)

Cycle	BET Area ($m^2\ g^{-1}$)	Pore Volume ($cm^3\ g^{-1}$)
Fresh	1,391 ± 26	0.66
1	1,102 ± 21	0.65
2	1,076 ± 19	0.62
3	869 ± 15	0.54
4	757 ± 11	0.48

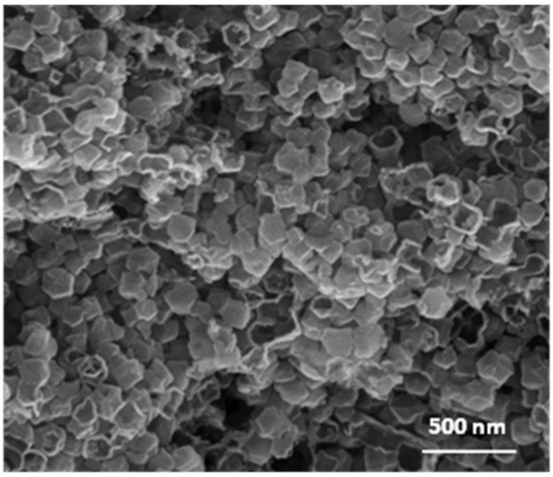

Fig 10. SEM image of activated ZIF-8 after fourth run of catalytic reaction.

Finally, even if the highest yield to methyl lactate from sucrose (around 42 %) reached here is below the yields reported for Sn-Beta zeolite (64 %) [14] and Sn-MCM-41 (43 %)[21], the present work is not only interesting because of the relatively good performance of the ZIFs but also because new opportunities in which MOFs may have useful applications in biorefinery emerging processes.

4. Conclusions

ZIFs were used for the first time in the transformation of sugars to lactic acid derivatives, such as methyl lactate, with high conversion and yield. ZIF-8 and ZIF-67 were synthesized following a previously developed method. Although both solids had the same sodalite type structure, their behavior as catalysts in sugar conversion was different. ZIF-67 was found not to be efficient for the process; however, ZIF-8 gave a better catalytic performance than its corresponding metal salt. Thus ZIF-8 was found to be an active and selective catalyst for the conversion of sugars into methyl lactate. The optimum reaction conditions were 24 h at 160 ºC using 160 mg of catalyst. Although methyl lactate was not the only product detected, a high yield was observed.

The use of sucrose as substrate provided the best catalytic results with ZIF-8. Besides, ZIF-8 could be reused for at least four cycles with methyl lactate yield drop from 34.8% in the first cycle to 27.2 % in the fourth cycle.. An activation process of the catalyst was needed between runs due to some compounds being adsorbed during the reaction and some chemical, textural and morphological effects occurring, as evidenced by the characterization carried out. Finally, it should be noted that MOFs, with their highly desirable and tunable structural, textural, morphological and compositional properties, would be attractive materials for use as catalysts in the heterogenization reaction of sugars to produce methyl lactate, and similar processes.

5. Acknowledgments

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SUPPORTING INFORMATION

Chemocatalysis of sugars to produce lactic acid derivatives on zeolitic imidazolate frameworks

Beatriz Murillo[1], Beatriz Zornoza[1], Oscar de la Iglesia[2], Carlos Téllez[1]*, Joaquín Coronas[1]

[1]Department of Chemical and Environmental Engineering and Instituto de Nanociencia de Aragón (INA), Universidad de Zaragoza, 50018 Zaragoza, Spain.

[2]Centro Universitario de la Defensa Zaragoza, Academia General Militar, 50090 Zaragoza, Spain.

*Corresponding author: Dr. Carlos Téllez. Universidad de Zaragoza. c/ Mariano Esquillor s/n. 50018 Zaragoza. Spain. Phone: 34 976 762897. Fax: 34 976 761879. e-mail: ctellez@unizar.es

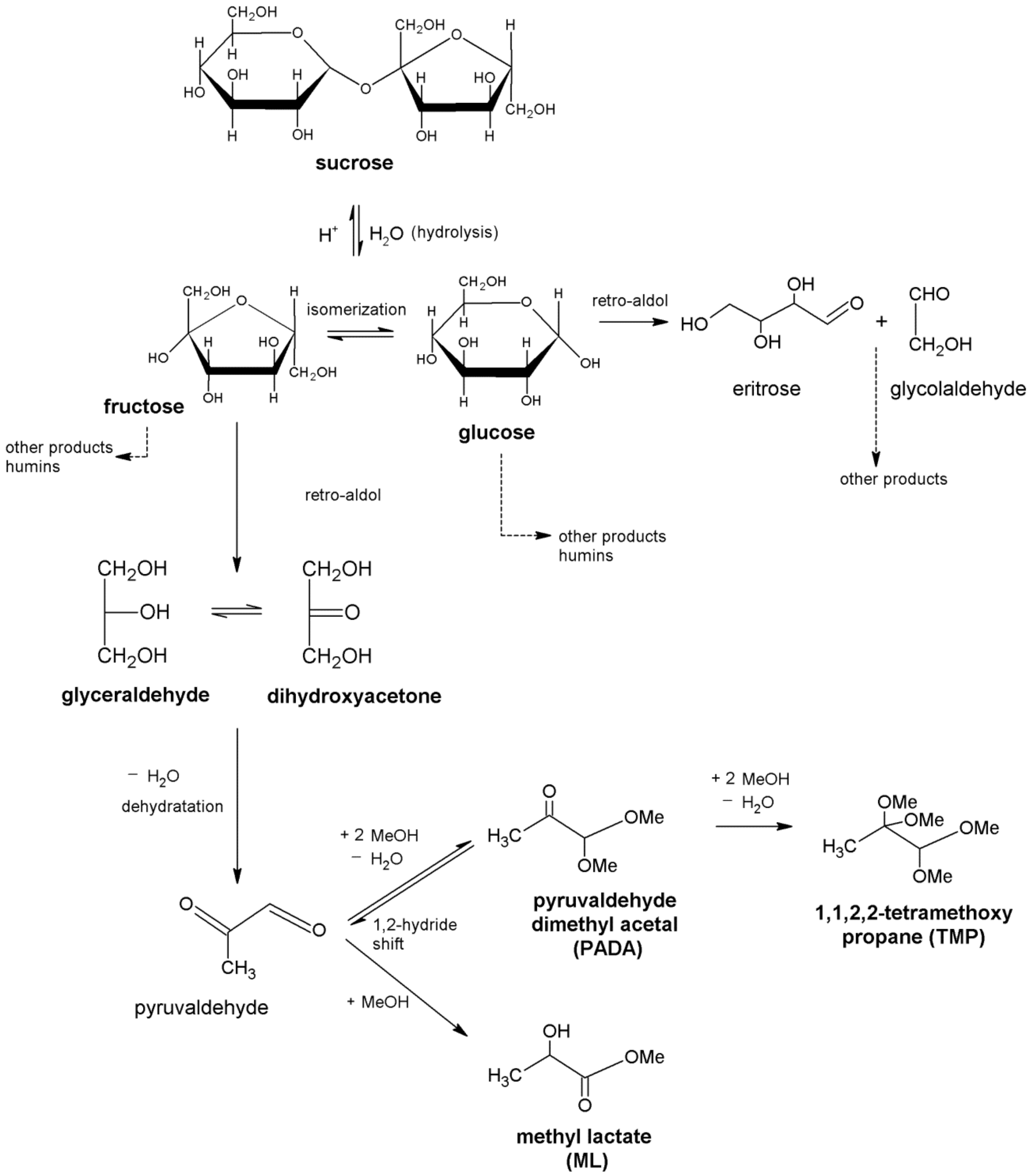


Figure S1. Possible pathway for the conversion of sucrose to methyl lactate using ZIF-8 based on mechanism on references [1-2].

Figure S2. Picture of the rotatory oven used in the catalytic conversion of sugars reaction.

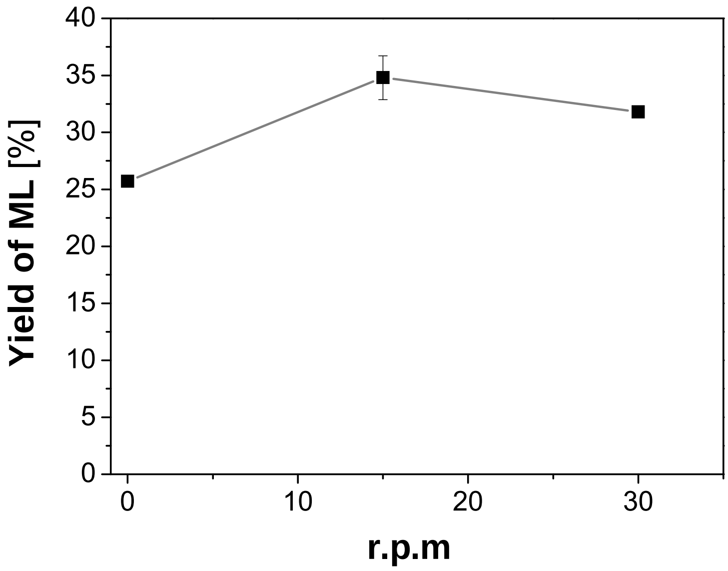


Figure S3. Yield of methyl lactate (ML) obtained over ZIF-8 using different revolutions per minute (r.p.m) in the rotatory oven. (Reaction conditions: 160 ºC, 160 mg of catalyst and 225 mg of sucrose).

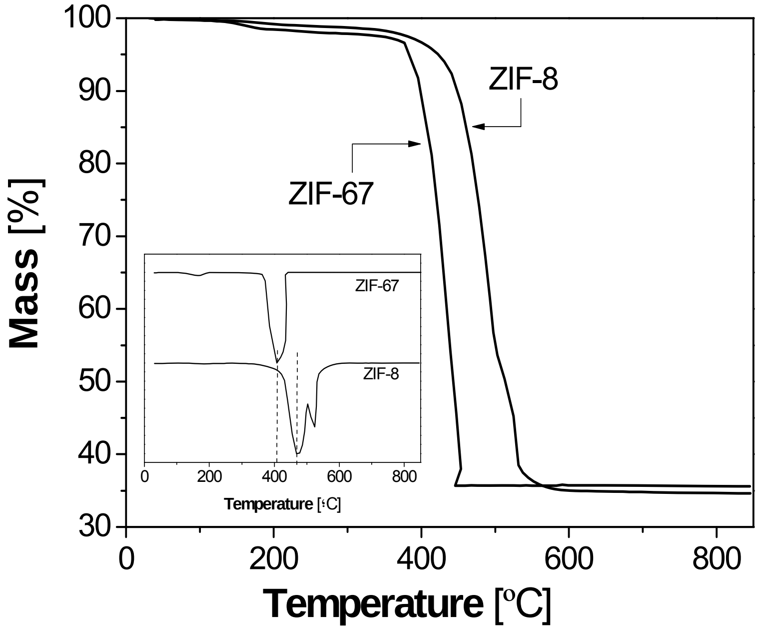
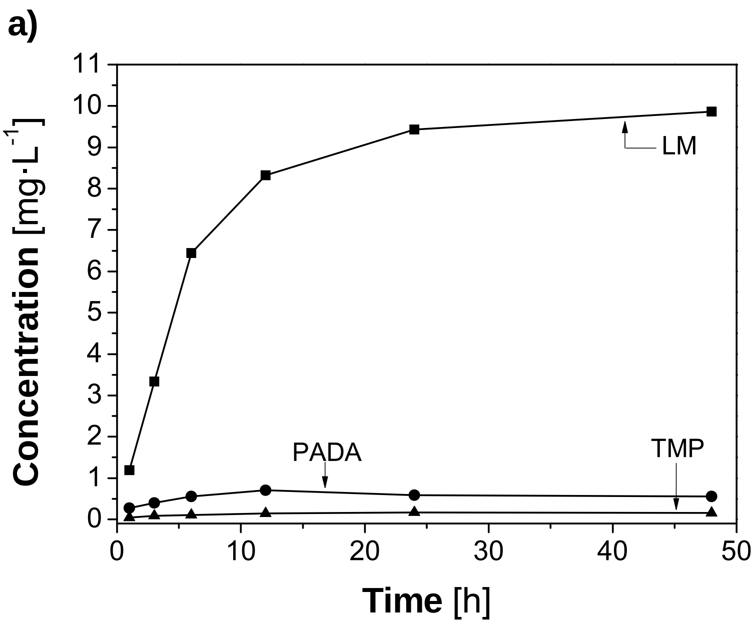
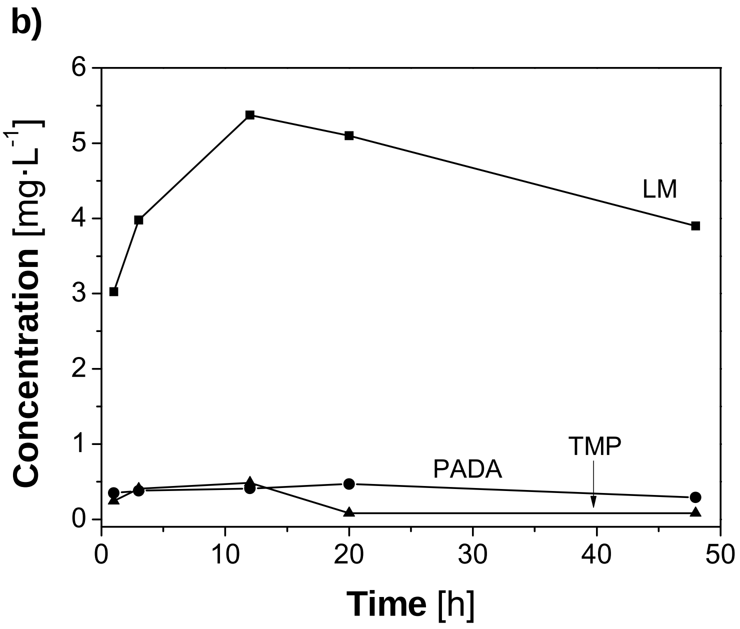


Figure S4. TGA curves and derivatives of 'as-synthesized' ZIF-8 and ZIF-67.





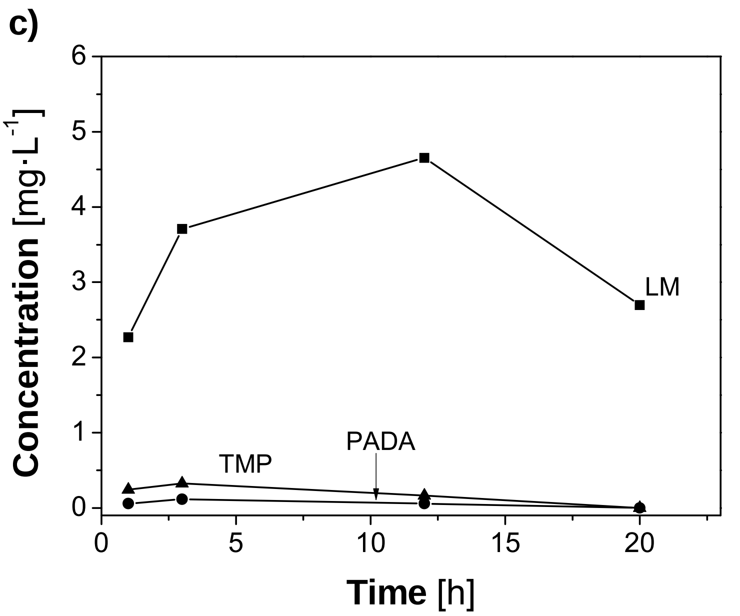


Figure S5. Concentration profile of analyzed products obtained over ZIF-8 using different sugars as reactants: a) Sucrose. b) Glucose. c) Fructose. (Reaction conditions: 160 ºC, 160 mg of catalyst and 225 mg of sugar).

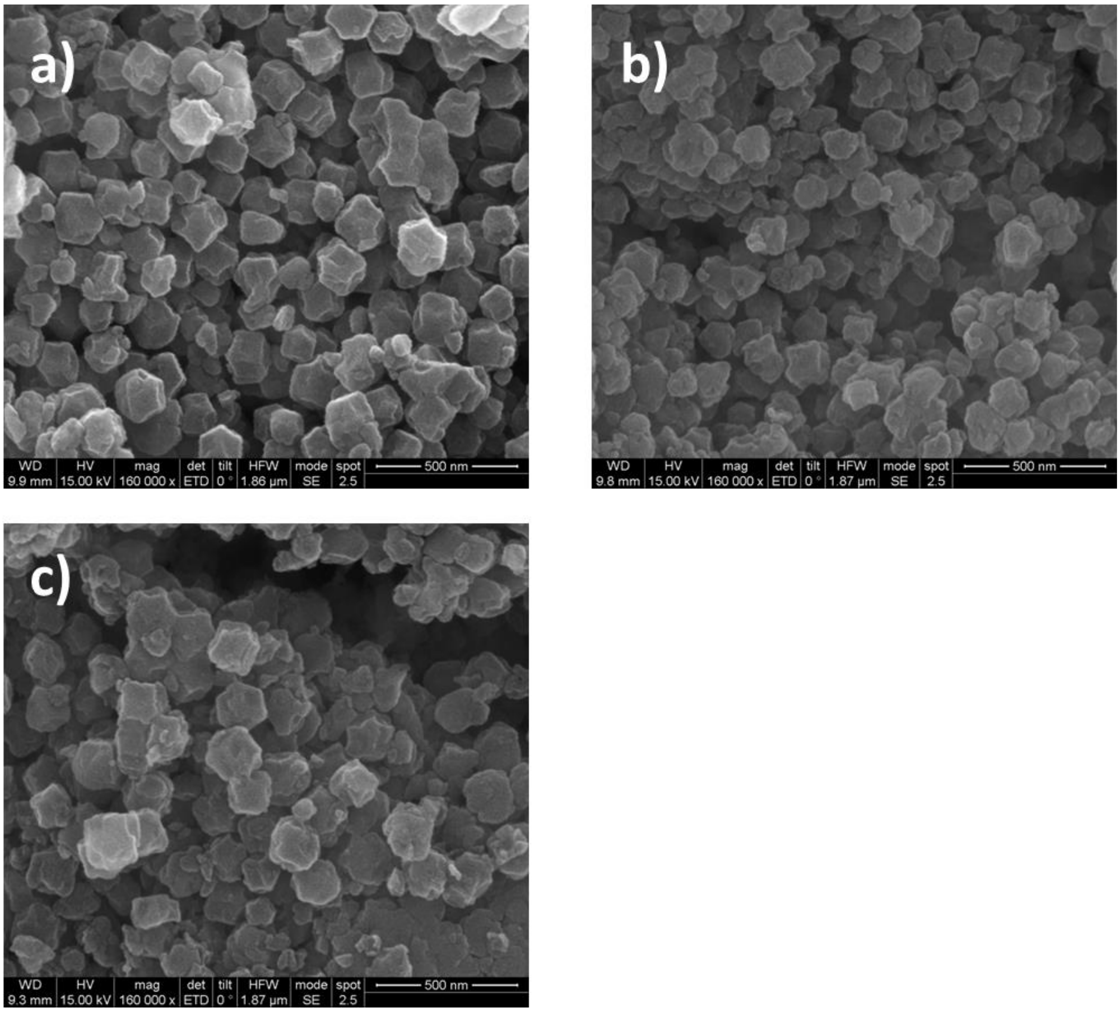


Figure S6. SEM images for activated recovered solid after each run: (a) recovered solid after 1st run, (b) recovered solid after 2nd run, (c) recovered solid after 3rd run.

Table S1. Errors for yield values obtained for sugar transformation with different catalysts. Methyl lactate (ML), pyruvaldehyde dimethyl acetal (PADA), 1,1,2,2-tetramethoxypropane (TMP) and non-identified products (n.i.p.).. Errors entries 1-7, 10, 11 from different experiments (at least 3). Errors entries 8, 9, 12, 13 analysis error. Reaction conditions: 24 h, 160 mg of catalyst and 225 mg of sugar. [a]Reaction time: 20 h.

Entry	Catalyst	Substrate	Yields (%)			
			ML	PADA	TMP	n.i.p.
1	Blank	Sucrose	1.4 ± 0.9	2.5 ± 1.4	0.1 ± 0.04	4.3 ± 1.3
2	Blank	Glucose	1.1 ± 0.7	2.5 ± 1.2	-	6.0 ± 1.7
3	$Zn(NO_3)_2 \cdot 6H_2O$ [a]	Sucrose	22.1 ± 4.5	1.4 ± 1.1	0.6 ± 0.05	3.5 ± 1.2
4	$Zn(NO_3)_2 \cdot 6H_2O$ [a]	Glucose	19.6 ± 3.6	2.4 ± 1.5	0.3 ± 0.01	2.5 ± 1.3
5	$Co(NO_3)_2 \cdot 6H_2O$ [a]	Sucrose	25.9 ± 2.3	0.2 ± 0.01	0.1 ± 0.02	1.2 ± 0.7
6	$Co(NO_3)_2 \cdot 6H_2O$ [a]	Glucose	23.0 ± 2.1	-	-	1.2 ± 0.9
7	ZIF-8	Sucrose	34.8 ± 1.9	1.9 ± 1.1	0.4 ± 0.02	3.3 ± 1.2
8	ZIF-8 [a]	Glucose	19.8 ± 2.6	0.8 ± 0.1	0.1 ± 0.03	2.0 ± 1.5
9	ZIF-8 [a]	Fructose	10.5 ± 2.2	-	-	1.5 ± 1.2
10	ZIF-67	Sucrose	19.1 ± 2.3	0.1 ± 0.03	0.1 ± 0.01	2.4 ± 1.8
11	ZIF-67	Glucose	10.4 ± 1.6	0.2 ± 0.01	0.1 ± 0.02	2.0 ± 1.2
12	ZIF-8	Sucrose	6.1 ± 0.2	0.1 ± 0.04	0.2 ± 0.05	9.1 ± 3.3
13	ZIF-8	Sucrose	2.2 ± 0.3	-	-	7.2 ± 4.6

Table S2. Energy Dispersive X-Ray (EDX) Analysis. This system is an attachment to Scanning Electron Microscopy (SEM).

Sample	Atomic ratio	
	N/Zn	C/Zn
ZIF-8	4.4	10.5
Activated recovered solid after 1st run	3.9	10.9
Activated recovered solid after 2nd run	2.7	10.1
Activated recovered solid after 3rd run	2.3	8.3
Activated recovered solid after 4th run	1.1	8.4

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