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

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ABSTRACT

Several research studies related to biorefining have focused on developing routes for biomass conversion into biomaterials or platform molecules. In this work, the zeolitic imidazolate frameworks (ZIFs) 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).

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

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pointed out that direct obtaining of methyl lactate has some advantages in front of lactic acid, due to the fact that an esterification step and a hydrolysis stage are needed for lactic acid purification [5]. Besides methyl lactate is a lactic acid precursor, and it has its own applications such as green solvent.

Metal–organic frameworks (MOFs) are crystalline hybrid compounds formed by metal clusters 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, they are easy to obtain, 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 × 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 levulinate yields [57]. Other authors have functionalized MOFs for fructose conversion [58,59] and glucose isomerization [60].

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.

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 °C 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 40 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

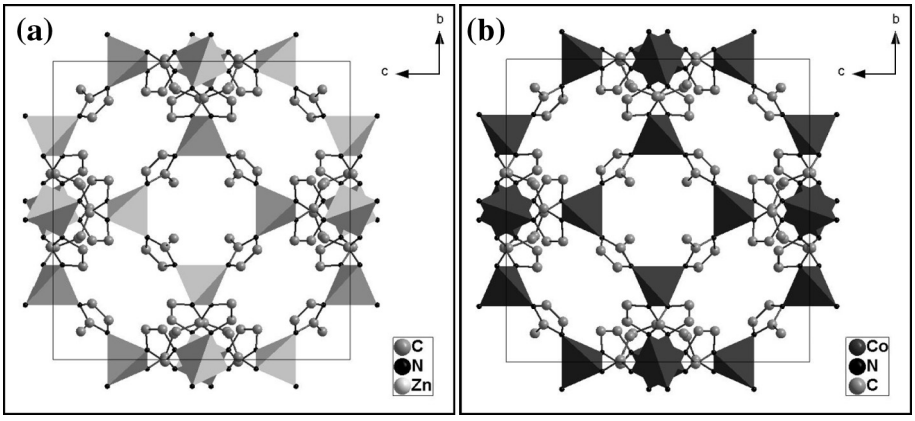

Fig. 1. Representation of ZIF-8 (a) and ZIF-67 (b) frameworks using Diamond 3.2 software. Crystal data from CCDC (The Cambridge Crystallographic Data Centre): ZIF-8 (CCDC code VELVOY) [44]; ZIF-67 (CCDC code GITTOT) [45].