

Review

Heterogeneous Catalysts for the Conversion of Glucose into 5-Hydroxymethyl Furfural

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Abstract: Lignocellulosic biomass, a cheap and plentiful resource, could play a key role in the production of sustainable chemicals. The simple sugars contained in the renewable lignocellulosic biomass can be converted into commercially valuable products such as 5-hydroxymethyl furfural (HMF). A platform molecule, HMF can be transformed into numerous chemical products with potential applications in a wide variety of industries. Of the hexoses contained in the lignocellulosic biomass, the successful production of HMF from glucose has been a challenge. Various heterogeneous catalysts have been proposed over the last decade, ranging from zeolites to metal organic frameworks. The reaction conditions vary in the reports in the literature, which makes it difficult to compare catalysts reported in different studies. In addition, the slight variations in the synthesis of the same material in different laboratories may affect the activity results, because the selectivity towards desired products in this transformation strongly depends on the nature of the active sites. This poses another difficulty for the comparison of different reports. Furthermore, over the last decade the new catalytic systems proposed have increased profoundly. In this article, we summarize the heterogeneous catalysts: Metal Organic Frameworks (MOFs), zeolites and conventional supported catalysts, that have been reported in the recent literature and provide an overview of the observed catalytic activity, in order to provide a comparison.

Keywords: biomass; HMF; 5-HMF; glucose; MOF; zeolite; Sn-Beta; dehydration; isomerization



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1. Introduction

The development of renewable fuels and chemicals have been the topic of active research for decades. This drive towards sustainability is fuelled by global warming. It has been proposed that plant biomass, a cheap and plentiful resource, could play a key role in the production of sustainable chemicals by the future biorefinery. Plant biomass consists of simple sugars, and can be converted into commercially valuable products such as 5-hydroxymethylfurfural (HMF) [1,2]. HMF is a potential platform molecule to realise the biorefinery concept because it can be transformed into numerous chemical products that have usage in a wide variety of industries (Figure 1). Several excellent reviews have been reported in the literature covering the HMF production from biomass resources [3–6].

Plant biomass is mainly made up of cellulose, hemicellulose, and lignin. The most common sugar found in cellulosic biomass is glucose. The conversion of glucose into HMF presents challenges. The difficulties that need to be overcome can be listed as follows: (i) the catalytic processes that show reasonable activity use hazardous reaction solvents; (ii) the synthesis of catalysts used in the proposed processes can only be synthesised by toxic solvents, and/or under high temperature and pressures from expensive compounds that makes them difficult to scale-up for industrial production levels; (iii) the selectivity of HMF is low and it is accompanied by undesired side products which makes the separation of HMF difficult and expensive; (iv) the heterogeneous catalysts generally have poor hydrothermal stability and thus deactivate rapidly. These drawbacks are preventing the

realisation of an industrial glucose-to-HMF production. A desired catalytic system suitable for an industrial scale production should ideally have the following properties: (i) it should operate in green solvents, preferably in water; (ii) the synthesis of the catalyst should be scalable and should involve only non-toxic chemicals—ideally, the catalyst should be a commercially available material or a simple variant of a commercially available material; (iii) the process should be selective towards HMF to minimise the separation costs; (iv) finally, milder reaction conditions, e.g., temperature < 120 °C and at ambient pressure, are preferable to minimise the scale up and operating costs.

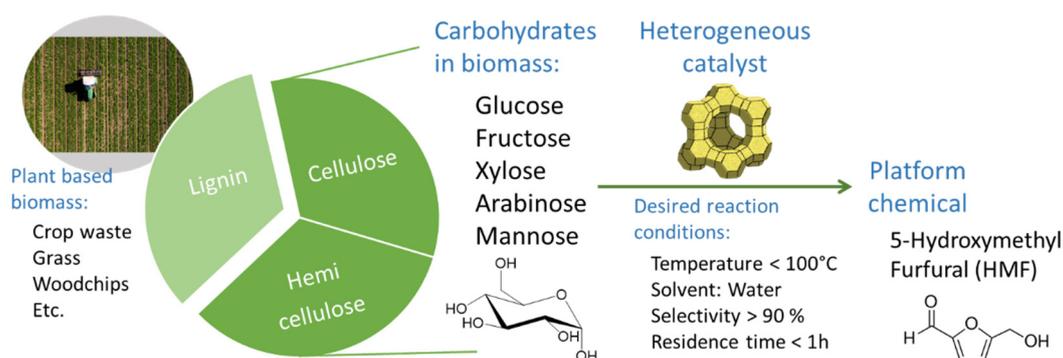


Figure 1. The schematic representation of the conversion of biomass and its major constituent sugars into HMF.

To achieve these objectives, it is essential to understand the mechanism of this transformation. Kinetic and mechanistic studies in the literature on various catalytic and non-catalytic systems reveal the details of glucose conversion through various pathways. These studies provide clues for researchers to develop new catalytic systems to remove the obstacles of the path to an industrial process. Various heterogeneous catalysts have been proposed in the literature, which are operating in numerous different process parameters. The catalysts used in these proposed catalytic systems can be classified as: (i) zeolites, (ii) metal organic frameworks, and (iii) supported metal oxides. First, we discuss the mechanism and kinetics of glucose conversion. Then, classes of catalysts are discussed and the recent reports are summarised.

2. Mechanism of Glucose Conversion

Fructose can be readily dehydrated to HMF. For instance, the production of fructose derived HMF can be effortlessly achieved by autocatalytic systems at elevated temperatures [7]. As catalysts are considered, both homogeneous and heterogeneous acid catalysts have been widely reported in the literature to produce HMF from fructose with yields exceeding 90% [3]. On the contrary, the conversion of glucose to HMF remains challenging. The HMF yields are low, and it is accompanied by side products. The conversion of glucose to HMF proceeds most likely through fructose as being the intermediate (Figure 2). In other words, first glucose is isomerised to fructose, and the in situ produced fructose is dehydrated to HMF as soon as it is formed in the reaction environment. Therefore, the bottle neck for high HMF yield from glucose remains at the first reaction step, i.e., the isomerisation of glucose to fructose in high selectivity.

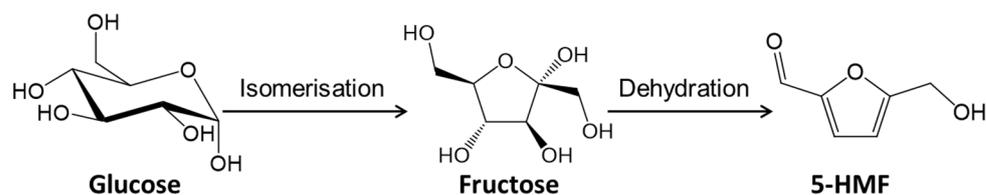


Figure 2. Chemical pathway of glucose conversion to HMF.

Chromium (II) chloride (CrCl_2) in ionic liquid-ethyl methyl imidazolium chloride (EMIMCl) was reported in 2007 by Zhao et al. [8], which showed an unprecedented selectivity of HMF production from glucose. From this example the mechanism for the conversion of glucose into HMF can be easily explained. In this homogeneous catalytic system, Cr(II) ions were able to convert glucose into HMF with a yield close to 70% at a glucose conversion above 90% in 3 h at 100 °C. The singular effectiveness of Cr^{2+} ions was not clear at that time. Later, we demonstrated that there is a peculiar coordination between the Cr^{2+} and glucose that happens only during the reaction [9]. The Cr^{2+} were shown to be self-organising into a binuclear structure impermanently. The peculiar activity of CrCl_2 in EMIMCl is due to its ability to isomerise glucose into fructose. The mechanism of this conversion starts with the ring opening of glucose. The ring opening is evidenced by the observation of mutarotation of alpha-glucose into beta-glucose, which only occurs through ring opening. The next stage is the proton (H^+) transfer from C2 to C1 (Figure 3).

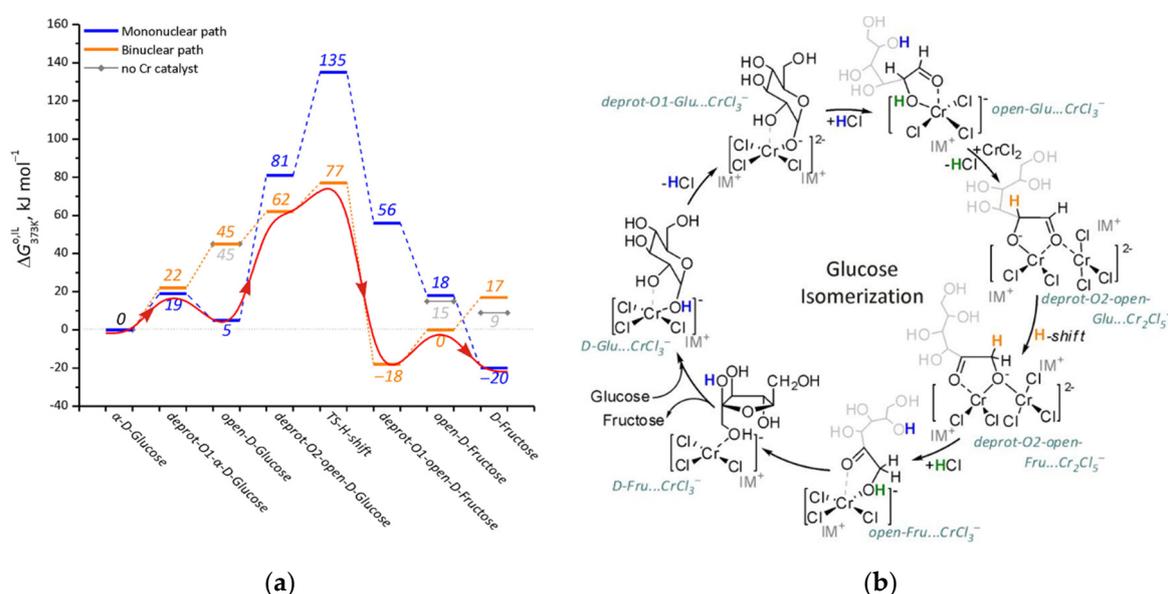


Figure 3. Calculated reaction energy diagrams (a) for glucose isomerisation mechanism involving a mono or a binuclear Cr(II) complex in a model MMIM ionic liquid media. The red line shows the lowest free energy path with the respective catalytic cycle shown on the right (b). Reproduced from “Glucose Activation by Transient Cr^{2+} Dimers by E. A. Pidko, V. Degirmenci, R. A. van Santen, E. J. M. Hensen, *Angew. Chem. Int. Ed.* 2010, 49, 2530-2534” [9]. © 2021 with permission from John Wiley and Sons.

The chlorine ions of the ionic liquid form a hydrogen bonding network with the hydroxyls of glucose, and as being basic, the Cl^- ions facilitate the proton transfer. The isomerisation of glucose into fructose occurs by the H^+ transfer from C2 to C1, which requires the deprotonation of O2-H group. This step requires a high activation energy when there is one metal coordinated to glucose. Conversely, the activation energy decreases significantly in the presence of a binuclear Cr-Cr complex. The formation of this binuclear complex is evidenced by the in situ Extended X-Ray Absorption Fine Structure (EXAFS) study which was supported by the activation energy calculations by density functional theory (DFT). Interestingly, the binuclear complex does not last in the next step of the mechanism that is the ring closure revealing fructose. The Cr ions as a binuclear complex stabilise the reaction intermediates involving the proton shift and the moderately basic Cl ions promote the deprotonation and protonation steps. This leads to the efficient isomerisation of glucose into fructose followed by fructose conversion into HMF, where the HMF selectivity is determined by the glucose isomerisation into fructose. We have later showed that a similar reaction mechanism is prevalent when other metal ions, such as iron (Fe) and copper (Cu) are used [10,11]. A similar reaction environment can be replicated on

the surface of a heterogeneous catalyst [12,13]. However, the impermanent binuclear Cr complex in [EMIM]Cl is unique where the Lewis acid Cr sites provide the selectivity for glucose isomerisation. Meanwhile the Brønsted acidity enhances the conversion rates by (i) boosting the proton network in the reaction medium enhancing the glucose isomerization rate to fructose, and (ii) facilitating the dehydration of fructose to HMF. The understanding of the reaction mechanism for glucose isomerisation is essential to achieve the objectives for the development of a highly desired effective heterogeneous catalyst. One of the most effective heterogeneous catalyst enabling the selective isomerisation of glucose into fructose is Sn-Beta zeolite. The heterogeneous Lewis acid Sn-Beta zeolite was reported to catalyse the glucose isomerization into fructose in water selectively [14–16] and it is followed by numerous mechanistic studies in the literature. In this catalyst, the Sn metals are isolated as Lewis acid centres in a relatively hydrophobic alumina silicate molecular cages of zeolite Beta. It is widely agreed in the literature that the intrinsic hydrophobicity of the cages of zeolite Beta plays an important role in the selective conversion of glucose. The hydrophobic surface could limit the excessive diffusion of water in the micropores [17], thereby the catalytically active sites are protected from deactivation. In addition, it allows the fructose and HMF to diffuse out of the cages when the reaction is complete without further conversion into undesired side products. In other words, the limited availability of water inside the zeolite beta cages prevents the reaction intermediates to change their coordination due to the surface adsorbed water to form undesired side products instead of fructose and HMF.

Studies for revealing the nature of the active Sn sites in Beta zeolite widely agreed on the existence of two types of sites for Sn-Beta [18–20] (Figure 4). The first site, named as the closed site, contains Sn connected to four O–Si groups. The partial hydrolysis of this site could generate another type of environment around the Sn atoms. The so called open site is where Sn is connected to three O–Si groups ((SiO)₃Sn(OH)) with an adjacent silanol group (Si–OH) [21]. The isomerisation of glucose into fructose takes place on the open sites of Sn-Beta. The reaction mechanism follows the same steps as in homogeneous CrCl₂ in ionic liquid catalytic system. The ring opening of glucose is followed by the endothermic intramolecular proton transfer step. The hydroxy groups attached to the Sn metal ((SiO)₃Sn(OH)) can act as Brønsted base which lowers the activation energy for the initial deprotonation of glucose. Next, the cooperative action of a Sn metal and an adjacent proton donor site can stabilise the transition state during the proton transfer between C1 and C2. In the zeolite beta cage, the hydrophilic Beta framework limits the deactivation of these active sites by contact with bulk water. During the intramolecular proton shift between C1 to C2 carbons of glucose, the open-chain glucose molecule coordinates to Sn in monodentate form. Meanwhile, it is coordinated to the adjacent silanol group through hydrogen bonding. This intermediate chemical environment leads to isomerisation of glucose into fructose. On the other hand, the coordination of glucose to Sn open site in a bidentate fashion favours the epimerisation. In this chemical coordination environment, the adjacent silanol is spectator. The epimerisation forms mannose through a carbon shift. Local environment around Lewis acid (Sn) sites and hydroxyl density of zeolite framework at the surface is crucial for activity and selectivity in this reaction [20,22].

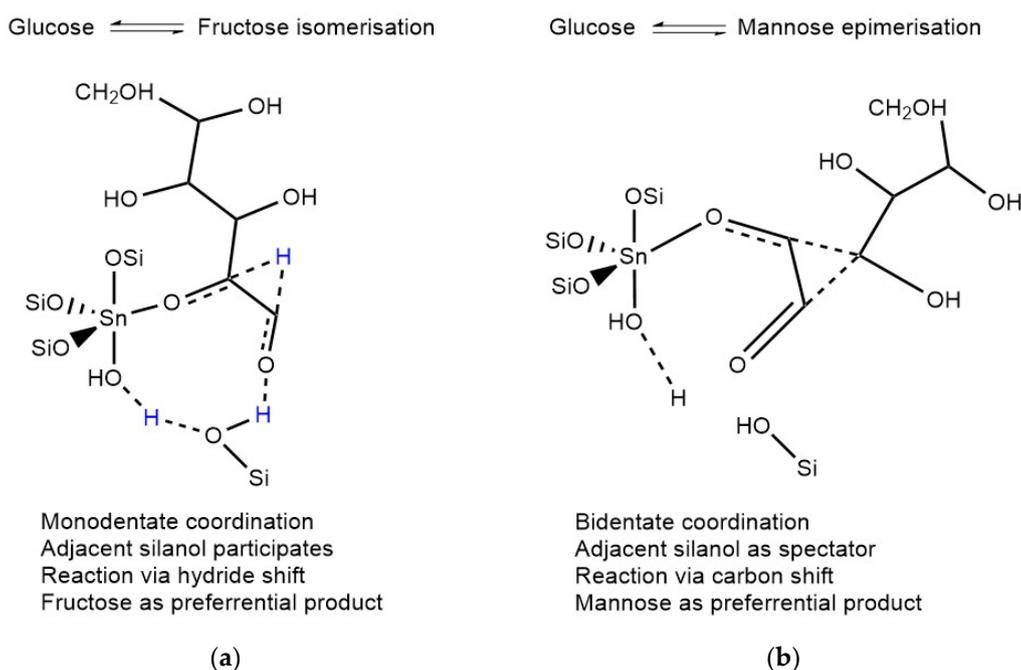


Figure 4. Sn-Beta transition states in the (a) isomerisation of glucose to fructose and (b) epimerisation of glucose to mannose. Reproduced from “Catalytic Isomerization of Biomass-Derived Aldoses: A Review”, by I. Delidovich, R. Palkovits, *ChemSusChem* 2016, 9, 547–561 [18]. © 2021 with permission from John Wiley and Sons.

The most common overall reaction pathways that have usually been reported in the literature involve the three products, fructose, mannose and [14,15,23] HMF (Figure 5). The isomerisation of glucose to fructose proceeds over a Lewis acid catalyst, and mannose can be produced as a by-product through epimerisation. The dehydration of fructose to 5-HMF is catalysed by Brønsted acids. In addition to the products of fructose, mannose and HMF, several by-products could also form in glucose conversion reactions, and thus the mass balances are often not closed. The main by-product is the poorly characterised oligomers, named as humins [24]. These are short chain polymeric products, which are insoluble in water, that usually entrapped on the active sites when the reaction system is a heterogeneous catalytic system. The potential by-product reaction pathways starting from glucose is numerous [23]. Therefore, simplified reaction schemes are usually used in the literature to model the reaction system and estimate the reaction kinetic parameters. In general, retro-aldolization of glucose, fructose or mannose and the formation of lactic acid, furfural, and levulinic acid are commonly observed as products in addition to humins [3]. The HMF itself and the reaction intermediates are clearly highly reactive. This makes it difficult to design a catalyst for selectively reduce the activation energy of a route leading to HMF. The sensitivity of the reaction to slight changes in temperature is therefore evident. The precise control of temperature and other operating parameters could be essential to eliminate the side product formation in an industrial scale application. Thus, non-traditional novel reactor designs which allows precise temperature control such as radio frequency heating [25–27] could be a game changer in future for HMF production.

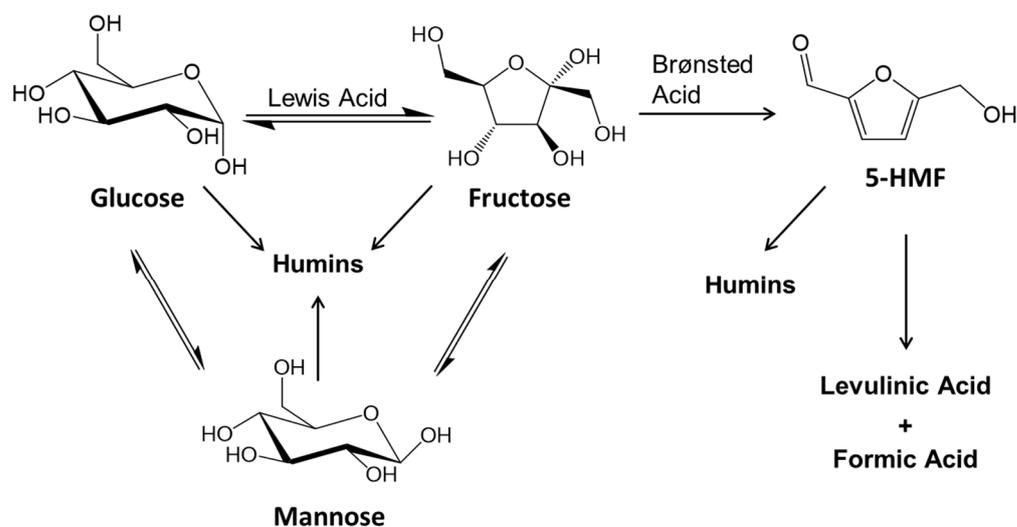


Figure 5. The overall reaction scheme of glucose conversions, showing glucose isomerisation to fructose, epimerisation to mannose and the formation of side products.

The unique feature of the coordination of Cr(II) ions of glucose in ionic liquid and the delicate nature of the active site in Sn-Beta zeolite evidences the importance of the fine tuning of the structure of catalysts for efficient glucose utilisation. Understanding of the structure-activity relationships is the key point to elaborately design an efficient catalyst with desired functionality for improving its selectivity at high conversion rates towards the desired product, HMF. Below we summarise the heterogeneous catalysts reported in the recent literature enabling this transformation. We grouped them into three categories, (i) zeolites, (ii) MOFs, and (iii) conventional supported catalysts.

3. Zeolites

A large effort has been spent on the development of the catalytic sites within the complex environment of zeolites. Zeolites are a diverse family of crystalline aluminosilicates, composed of a network of interconnected micro pores and cavities [28,29]. The framework consists of interlocking, corner-sharing tetrahedrons of SiO_4 and AlO_4 . These are joined together in varying regular arrangements via shared oxygen atoms and form a network of pores (Figure 6). Zeolites are widely used as heterogeneous catalysis, with broad use in the oil refining sector. Their high thermal and mechanical stability, high surface areas, tuneable pore sizes and shapes and changeable surface properties makes them a suitable class of materials for various catalytic applications.

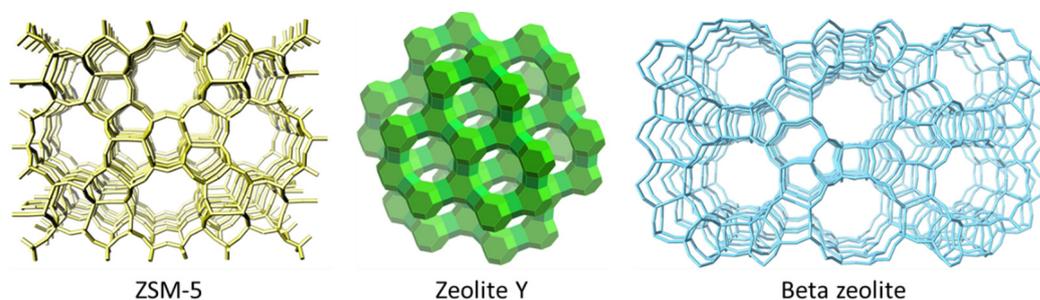


Figure 6. Representative zeolite structures; ZSM-5, Zeolite Y and Beta zeolite.

In the early 2010s several reports discussed the high activity of Sn sites that have been incorporated into the framework of zeolite beta [14,30,31]. The direct incorporation of the Sn species into the zeolite framework in a one pot synthesis procedure [32,33] is time consuming (40 days). Moreover, the synthesis requires the use of HF which is not preferable due to its high toxicity. Alternative procedures have been published to incorporate the Sn

by fast post-synthesis procedures [34–37]. For instance, Van der Graaff et al. [38] described the synthesis in which Sn species were introduced into the zeolite framework post-synthesis by dealumination followed by grafting SnCl₄ precursor. This synthesis method reduces the preparation time of Sn-Beta substantially without losing sacrificing its catalytic activity. The Sn^{IV} in the zeolite lattice replacing the T4 atoms of the zeolite beta framework with the hydroxylated Sn–OH species in close proximity of silanol nests [39] are the active species. It has been shown that it is possible to introduce other metals forming similar chemical environment such as, Nb [40], Ti [37,41] and Zr [37]. These metals in zeolite beta are shown to be active in glucose isomerization too.

Besides the chemical properties of the Sn species the high activity of the Sn-Beta catalyst has been attributed to the pore topology of the zeolite structure providing the required activity [42]. Various Sn containing zeolites were functionalized with Sn species and it was shown that the larger pore zeolite frameworks BEA and MOR (12 membered rings) showed much higher activity compared to slightly narrower medium pore zeolites (10 membered rings) such as MWW and MFI frameworks. The lower activity was attributed to the strong confinement in these medium pore MWW and MFI zeolites. Furthermore, the bulkiness of the carbohydrate molecules introduces diffusion limitations, which increase with smaller pore diameters. Later work also showed that the micropore system of Sn-Beta is prone to catalytic deactivation due to the deposition of oligomerization (humins formation) originating from dehydrated carbohydrates [43]. The summary of zeolite-based catalysts for the conversion of glucose to HMF is given in Table 1.

Table 1. Zeolite heterogeneous catalysts, the conditions, and products in the conversion of biomass derived glucose to HMF.

Catalyst	T (°C)	Time (h)	Solvent	Glucose Conversion (%)	Product Yield (%)	Ref.
Sn-Beta	110	0.5	Water	55	Fructose: 32 Mannose: 9	[14]
Sn-Beta	160	1.5	pH = 1.0 HCl	45	Selectivity: HMF: 6	[44]
Sn-Beta	180	1.2	Phase 1: pH = 1.0 HCl and NaCl Phase 2: THF	79	Selectivity: HMF: 72	[44]
Sn-Beta	90	4	dioxane/water (95:5 w/w)	55	Fructose: 42	[45]
H-Beta	150	0.8	[BMIM]Cl	81	HMF: 50	[46]
Meso-Sn-MFI	80	2	Water	37	Fructose: 27 Mannose: 3	[47]
Nb-BEA	180	12	Phase 1: water and NaCl Phase 2: MIBK *	97	Selectivity: HMF: 84	[40]
Hierarchical Sn-Beta	160	3.5	DMSO: THF ** (3:7 v/v)	99	Selectivity: HMF: 42	[48]
Sn-Beta	160	3.6	DMSO: THF (3:7 v/v)	96	Selectivity: HMF: 32	[48]
Sn-Zeolite Y	140	3	Water	36	Fructose: 13 Mannose: 1 HMF: 4	[49]

Table 1. Cont.

Catalyst	T (°C)	Time (h)	Solvent	Glucose Conversion (%)	Product Yield (%)	Ref.
Ga-Zeolite Y	140	3	Water	17	Fructose: 5 HMF: 1.5	[49]
Sn-Zeolite Y	140	3	DMSO	66	HMF: 22	[49]
Ga-Zeolite Y	140	3	DMSO	78	HMF: 33	[49]
Cr-Zeolite Y	160	1.5	DMSO	Not stated	HMF: 35	[50]
Cr-Zeolite Y	130	1	*** [BMIM]Cl	Not stated	HMF: 59	[50]
H-MOR	100	6	[BMIM]Br	98	HMF: 32	[51]
H-MOR	65	9	Phase 1: acetone: water (3:2) Phase 2: Ethyl acetate (Phase 1: Phase 2 = 2:3 w/w)	98	HMF: 30	[51]
H-ZSM-5	195	0.5	Phase 1: water and NaCl Phase 2: MIBK (1.5:3.5 v/v)	80	HMF: 49	[52]
ZSM-5-SO ₃ H	140	4	DMSO:water (24:76 v/v)	70	HMF: 54	[53]

* Dimethyl sulfoxide (DMSO), ** Methyl isobutyl ketone (MIBK), Tetrahydrofuran (THF), *** 1-Butyl-3-methylimidazolium [BMIM].

The conversion of hexose carbohydrates into 5-HMF not only requires Lewis acid sites, but also Brønsted acid sites. The Lewis acid sites facilitate the isomerization of glucose to fructose, whereas the Brønsted acid sites enable the dehydration of the in situ formed fructose into 5-HMF. Therefore, various reports describe the use of a Lewis acid zeolites in combination with a homogeneous Brønsted acid catalyst or reaction medium. For instance, it was shown that the combination of Sn-Beta with HCl results in the formation of HMF from glucose in high yields [44]. However, the combination of both Lewis and Brønsted acidic properties in one heterogenous catalyst to perform this two-step reaction in one-pot is more desirable. In this respect, Al-beta was treated with steam to create partially defected framework and Lewis acid aluminium clusters outside the framework [54]. In this way a combination of both Brønsted and Lewis acid sites are present in the zeolite catalyst. The extra framework Alumina (Al₂O₃) possess Lewis acid character, whereas the framework aluminium atom is the factor making the nearby protons of hydroxyl groups strongly Brønsted acidic because of its electron withdrawing effect. The Al-beta showed an HMF selectivity of 55% at glucose conversion of 78% at 180 °C.

Saenluang et al. [55] took a different approach and introduced the Lewis acidic Sn during the synthesis of the hierarchical beta zeolite together with Al species without the use of HF. In this procedure hierarchical zeolite beta is treated using a cyclic quaternary ammonium salt as structure directing agent. A short hydrothermal procedure was required (24 h at 170 °C) to obtain a crystalline material which can obtain HMF in the direct conversion of glucose at 120 °C. Other metals in beta zeolite have been shown to be active in the direct conversion of glucose to HMF too. Candu et al. showed the high activity of glucose using a Nb post-synthesis modified beta zeolite. Selectivity of 87% to HMF were reached at glucose conversion of 97% at 120 °C.

Transport limitations reduce catalytic activity and increase the probability of humin formation which leads to catalyst deactivation. By reducing the micropore domains via introduction of mesopores, the diffusion length in the zeolite catalysts can be lowered [56,57] by maintaining the acidic strength and acid site amount of the original zeolite [27,58]. Yang et al. [48] showed the preparation of a hierarchical Sn containing beta zeolite. First the hierarchical Al containing beta zeolite is formed using a structure directing agent;

polydiallyl dimethyl ammonium chloride (PDADMA). Later, zeolite is dealuminated and SnCl_4 is introduced post synthesis. Catalytic evaluation showed substantially higher glucose conversion and HMF yield than the microporous Sn-Beta catalyst. Additionally, the hierarchical Sn-Beta showed high stability in recycle experiments.

Oozerally et al. [49] showed the possibility to introduce Sn and Ga metals via a post-synthesis procedure into zeolite Y. Advantage of the use of zeolite Y is the wide industrial application of the material thereby reducing the price and the presence of large sodalite cavities. It was shown that these materials show good activity when using DMSO as solvent without losing any activity. The Sn containing catalyst showed 17% HMF yield at a conversion of 36% during catalytic reaction at 140 °C. In water the materials deactivate possibly due to humin formation for the Sn containing catalyst, while the Ga containing Y zeolite probably deactivates due to Ga leaching. Another reason for the deactivation of the Sn containing Y zeolite could be the competitive adsorption of highly polar solvent molecules such as water to the Lewis acid sites present in zeolites which has previously shown by extensive C^{13} -NMR studies [59].

Although showing high activity, catalytic processes using zeolite are prone to deactivation. The formation of humin product originating from carbohydrates results in pore blockage. Cordon et al. [60] showed that the Sn-Beta deactivation is not only limited to the humin deposition. Instead, the structural changes are significant on the Sn-Beta structure in the presence of water, and the deactivation is closely related to the structural deformation and formation of silanol nests. Furthermore, when using water as the reaction medium, i.e., the reactant is aqueous glucose, many of these zeolite systems are prone to metal leaching from the zeolite framework [43]. Several studies showed that the zeolite materials are stable in solvents other than water. For instance, Sezgin [50] showed the beneficial effect of ionic liquids on the stability of Cr exchanged Y and beta zeolites. Similar results have been obtained for mordenite catalysts; however ionic liquids strongly adsorb in the micropore system of the micropores. Therefore, mesoporosity in zeolite framework has a positive effect on the catalytic activity [51]. However, the poor catalytic stability of mesoporous zeolites and the need for large number of organic solvents remain to be overcome to make the industrial application feasible. On the contrary to these findings, it is observed that the addition of traces of water into a methanol/sugar mixture enhances the stability of Sn-Beta zeolite. This is assigned to the hydration of Sn and Si sites and the formation and deformation of hydroxyls, e.g., Sn-OH, Si-OH [61]. Therefore, the presence of water is essential for the reaction kinetics to proceed to desired products with a delicate balance between activity and catalyst deactivation.

4. MOFs

Metal organic frameworks (MOFs) are a class of crystalline organic-inorganic hybrid compounds [62,63]. MOFs are formed by bonding of metal clusters or ions with organic linkers. The MOF crystals have high porosity, formed by uniformly sized pores (Figure 7). The selection of organic linkers and metal ions allows one to manipulate the intrinsic properties of MOFs. The possibility of using Metal Organic Framework (MOF) materials as catalysts in glucose dehydration has been investigated in various studies in the literature. The versatility of organic linkers in MOFs allows the controlled addition of Lewis and Brønsted acidic functionality into the framework. Moreover, the benefit of space confinement inside the pores could be achieved due to the porous structure of MOFs like that of zeolites. The three-dimensional structure of a MOF is created by the connection of metal atoms with organic linker molecules. The chemical and catalytic properties of the MOFs can be easily altered by adapting the chemical structure of the linker. This makes the MOFs high potential alternatives to be used as catalysts in the conversion of glucose to HMF. The morphology of MOFs resembles strongly to that of zeolites, with a distinction that MOFs are easier to prepare compared to their zeolite analogues. Furthermore, due to the high versatility of organic linkers their chemo catalytic properties are easily to adapt.

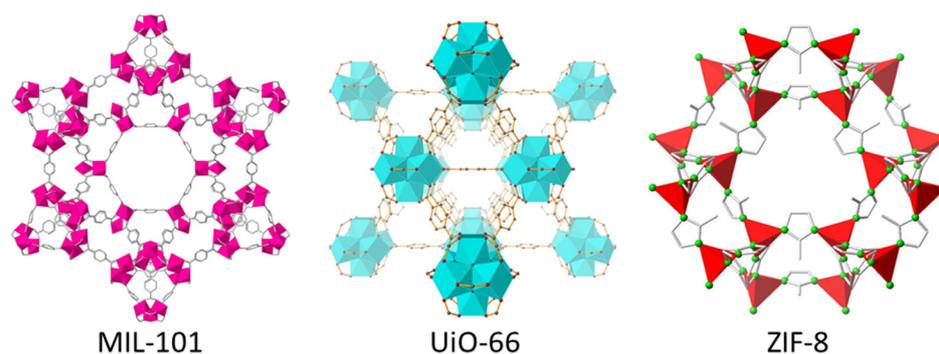
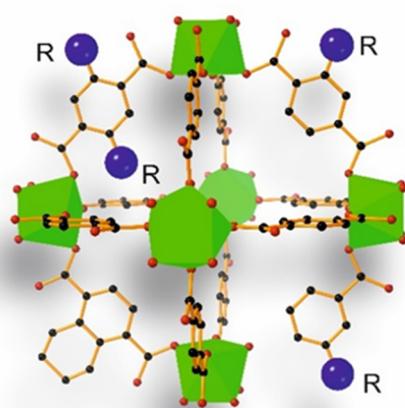


Figure 7. Representative MOF structures; MIL-101, UiO-66 and ZIF-8.

Oozerally et al. [64] exploited the versatility of MOFs and have shown the high activity and selectivity of ZIF-8 materials towards the isomerization of glucose to fructose. Zeolitic imidazolate frameworks (ZIFs) are a class of MOFs that are topologically isomorphic with zeolites. The ZIF-8 has Zn as the Lewis acidic metal centre facilitating the isomerization of glucose into fructose. To convert fructose to HMF through the dehydration reaction, Brønsted acidity is required. An example is a MIL-101 catalyst containing Cr as the Lewis acidic sites and a monosodium 2-sulfoterephthalate linker [65]. The linker provides the Brønsted acidity when the sulfonic group is exchanged to the H-form. This catalyst was shown to be active when glucose was converted in a mixture of THF and water at 130 °C. A maximum 5-HMF yield of 29% was achieved after 24 h of reaction in a 39:1 V/V ratio of THF and water. The same catalyst was used by different groups in a 10:1 γ -valerolactone:water mixture for the conversion of glucose. It showed a HMF yield of 44.9% [66].

The use of functionalised organic ligands as a linker for the synthesis of MOFs is a practical approach to decorate and introduce any desired functionality to the catalyst. UiO-66 was modified by this approach, and it has been shown as an exceptionally active and selective catalyst for the conversion of glucose to HMF [67]. Monosodium 2-sulfo-benzene-1,4-dicarboxylate (MSBDC) was used as the sulfonic acid containing linker. The sulphur groups on the linker provided Brønsted acid sites whereas the Zr in the framework of UiO-66 provided the required Lewis acidity. Testing the catalyst in the conversion of glucose at 140 °C, 3h resulted in a HMF yield of 22% at a glucose conversion of 32%. The overall selectivity of fructose and HMF over MSBDC-UiO-66 reached the same as Sn-Beta zeolite. In a follow up study, the versatility of the UiO-66 MOF has been demonstrated [68]. UiO-66 was synthesized by using various functionalised linkers (Figure 8). This allowed to vary various properties of the UiO-66 framework, such as the crystal size, electronegativity, basicity, Brønsted and Lewis acidity. Furthermore, it is shown that the UiO-66 MOF could be synthesized solely from the decorated organic ligands, such as NO₂(100)-UiO-66, NH₂(100)-UiO-66, Naphtha(100)-UiO-66, MSDBC(50)-naphtha(50)-UiO-66. The activity of these UiO-66 variants was reported to be active in HMF production in water, i.e., aqueous glucose, at 140 °C and stable in a flow reactor. The MSDBC(50)-naphtha(50)-UiO-66 catalyst showed overall product selectivity (fructose, mannose, HMF) of 55% at a glucose conversion of 33%.



**Decorated UiO-66
Metal Organic Framework**
R = SO₃H, NH₂, NO₂, CO₂H, OH

(a)

Catalyst	Conversion (%)	Yield (%)			
		Fructose	Mannose	HMF	Total
NO ₂ (20)-UiO-66	16.8	1.6	0.3	4.7	6.6
NO ₂ (50)-UiO-66	19.9	2.1	0.6	5.6	8.3
NO ₂ (100)-UiO-66	21.9	3	1.2	5.5	9.7
BTeC-UiO-66	20.9	2.0	0.3	7.3	9.7
IPA(10)-UiO-66	23.6	2.8	3.7	4.7	11.2
IPA(20)-UiO-66	23.6	2.7	3.6	4.5	10.8
IPA(30)-UiO-66	23.1	2.7	3.8	4.6	11.1
IPA(40)-UiO-66	24.4	3.1	4.1	4.9	12.1
NH ₂ (20)-UiO-66	16.7	2.2	1.4	3.9	7.5
NH ₂ (50)-UiO-66	19.0	1.9	1.2	5.2	8.3
NH ₂ (100)-UiO-66	15.9	0.9	0.2	5.5	6.6
Naphtha(20)-UiO-66	18.0	4.7	0.8	3.2	8.6
Naphtha(50)-UiO-66	18.2	5.5	0.9	3.1	9.5
Naphtha(100)-UiO-66	21.2	6.6	1.2	3.7	11.6
MSDBC(50)-naphtha(50)-UiO-66	32.7	7.1	5.4	5.4	17.9

(b)

Figure 8. Modification of UiO-66 framework (a) and corresponding activity of catalysts (b). Reaction conditions are: 140 °C, 3 h, substrate concentration of 10 wt %, Glucose to catalyst ratio of 30:1 by weight. Catalysts are coded with percent of modified linker in parenthesis, e.g., NH₂(50)-UiO-66 corresponds to catalyst prepared with 50% of the linker replaced with NH₂ modified linker. Reproduced from “Systematic Modification of UiO-66 Metal-Organic Frameworks for Glucose Conversion into 5-Hydroxymethyl Furfural in Water” by Oozeerally. et al. ChemCatChem 2021, 13, 2517–2529, (doi:10.1002/cctc.202001989) graphical abstract and Table 2, [68] CC BY.

Another UiO-66 material was tested in the glucose conversion under microwave heating at 160 °C for 30 min [69] using DMSO as the solvent. In this work HMF yields of ~20% were reached. A third type of MOF tested in glucose conversion to HMF is NU-1000, which makes use of Zr as the metal centre [70]. Although the catalyst was active in glucose conversion (60%) at 140 °C in water, the HMF yield was poor (2.3%) even after 5 h. After treating the MOF with phosphoric acid, a HMF yield of 65% was reached, which was however obtained in a 9:1 2-propanol/water mixture. Many of the reports concentrate on the use of Zr and Cr, however Riezzati et al. [71] have shown that Fe and La can be catalytically active too, when using DMSO as a solvent. The MOFs used in the conversion of glucose to HMF as heterogeneous catalyst are summarised in Table 2. The reaction conditions, conversion rates and product yields are given.

Table 2. MOFs as heterogeneous catalysts, the conditions, and products in the conversion of biomass derived glucose to HMF.

Catalyst	T (°C)	Time (h)	Solvent	Glucose Conversion (%)	Product Yield (%)	Ref.
UiO-66-SO ₃ H	140	3	Water	36	HMF: 8 Fructose: 22	[67]
MSBDC(50)-UiO-66	140	3	Water	37	HMF: 7 Fructose: 8 Mannose: 7	[68]
MSDBC(50)-naphtha(50)-UiO-66	140	3	Water	33	HMF: 7 Fructose: 6 Mannose: 6	[68]

Table 2. Cont.

Catalyst	T (°C)	Time (h)	Solvent	Glucose Conversion (%)	Product Yield (%)	Ref.
ZIF-8	100	3	Water	24	HMF: 16	[64]
MIL-88B(Fe,Sc)	140	3	DMSO	71	HMF: 25 Fructose: 3.3 Mannose: 1.4	[72]
Yb-BDC	140	24	Water	28	HMF: 18 Fructose: 1.2	[73]
La-BDC	130	6	DMSO	Not stated	HMF: 19	[71]
PTA-MIL-101(Cr)	100	3	[EMIM]Cl	21	HMF: 2	[74]
MIL-101(Cr)-SO ₃ H	120	2	DMSO	Not stated	HMF: 7	[75]
MIL-101(Cr)-SO ₃ H	120	2	[BMIM]Cl	Not stated	HMF: 8	[75]
MIL-101(Cr)-SO ₃ H	100	24	Water	22	Fructose: 22	[76]
MIL-101(Cr)-SO ₃ H	150	2	Phase 1: Water Phase 2: γ -valerolactone (1:9 w/w)	90	HMF: 40	[66]
MIL-101(Cr)-SO ₃ H	130	24	Phase 1: pH = 1.0 HCl and NaCl Phase 2: THF (1:39 v/v)	Not stated	HMF: 29	[65]
NU-1000	140	5	Water	60	HMF: 2.3 Fructose: 19	[70]
PO ₄ /NU-1000	140	5	Phase 1: Water Phase 2: THF (1:9 v/v)	97	HMF: 25 Fructose: 5	[70]
UiO-66-NH ₂ -SO ₃ H on g-C ₃ N ₄ @PDA	120	6	Isopropanol:DMSO (9:1 v/v)	92	HMF: 55	[77]

Besides the formation of bifunctional materials in the molecular structure of the MOF framework people have also investigated hybrid materials. Examples are Cr-OH particles on and within MIL-101(Cr) [78], UiO-66 supported on g-C₃N₄ [77] and phosphotungstic acid encapsulated MIL-101 [74]. Many reports on MOFs use a mixture of water and organic solvents. This is mainly due to the poor stability MOFs in aqueous glucose which results in catalyst deactivation and makes catalyst recycle impossible. One of the water stable MOFs showing activity in glucose conversion in pure water is a MOF prepared in a similar way as MIL-101 using Yb [73]. The final crystal structure though did not correspond to that of MIL-101. Over this MOF, after 24 h at 140 °C a HMF yield of 18% was reached at a glucose conversion of 28%. Furthermore, the material showed high stability in 24 h recycling experiments. The MIL-101 MOF is prepared with the toxic metal chromium. This is in analogy with the homogeneous CrCl₂ [EMIM]Cl ionic liquid which shows the highest HMF yield so far. However, the green chemistry practices need to be adopted for a future bio-renewables chemicals industry and thus such toxic metals should be avoided. For this purpose, a new type of MOF, prepared by replacing the Cr metals with Fe and Sc have been proposed [72]. This MOF in its bimetallic form is stable in DMSO and shows 35% HMF selectivity at 70% glucose conversion.

In summary, MOFs have high potential for the conversion of glucose into HMF because it is easy to modify the organic ligands in their framework. However, their poor hydrothermal stability in water causes the materials to degrade and, thus, deactivate rapidly. Further research is needed to improve their hydrothermal stability while maintaining their activity. Their microporous system makes them prone to deactivation because of active

site blockage by humin deposition, like in zeolite catalysts and the MOFs could only be reactivated by washing in liquid solvents to extract the humin deposits.

5. Conventional Supported Catalysts

Porous oxide supports such as SiO_2 and Al_2O_3 or resin materials such as Amberlyst-15 are more stable than MOFs and zeolites against deactivation, and thus they have a high potential to be used in an industrial process for glucose conversion. The use of Sn exchanged Amberlyst-15 was shown to be stable on the long duration conversion of glucose to 5-HMF at relatively low temperatures [79]. The preparation of the material requires a simple ion exchange step. The deposited Sn species provide the Lewis acidity required for glucose isomerization, while the sulfonic acid functionalized Amberlyst-15 provides the Brønsted acidity essential for fructose dehydration. Long duration continuous flow experiments revealed exceptional stability of this material in pure water as the solvent. In these packed bed flow reactor experiments, methyl isobutyl ketone (MIBK) was used as a second phase for the continuous extraction of hydrophobic products, mainly HMF. In a similar approach Amberlyst-15 was functionalized using Cr^{3+} species which showed high activity in a 9:1 wt/wt TEABr: water mixture [80]. High activity at lower temperatures is essential since the resin materials are not stable at higher temperatures [80–82]. Furthermore, resins have relatively low specific surface areas than porous zeolites and MOFs. Creation of porous resins, based on chitosan decorated with sulfonic acid groups on its surface was shown to improve the porosity of the material. This was achieved by creating Lewis acid Al^{3+} species [83].

Porous metal oxides as supports for catalysts have investigated widely, because of their potential high stability. In this respect, alumina (Al_2O_3) is a promising support, since it contains high porosity and Lewis acidity. However, using Al_2O_3 exclusively as a catalyst will not produce HMF because it lacks the Brønsted acidic sites required for the dehydration of fructose to HMF. Marianou et al. [84] investigated the use of Al_2O_3 supports impregnated with Sn. By doing so, they proved the necessity of strong Lewis acidic or Brønsted acidic sites to produce 5-HMF. Alternatively, incorporation of Zr into the Al_2O_3 framework via coprecipitation was studied. The Zr added Al_2O_3 catalyst showed reasonable activity to HMF (~45% yield at 175 °C) [85]. In a further attempt, Al_2O_3 was used as a catalyst in ionic liquids such as [EMIM]Br, where the ionic liquid provides the dehydration functionality [86]. For this catalytic system HMF yields of ~35% were achieved at 120 °C. However, the use of ionic liquids as a solvent is an expensive approach and thus makes the commercial application challenging to justify.

Unsupported amorphous Cr_2O_3 , SnO_2 , SrO and Fe_2O_3 metal oxides were all shown to be catalytically active in the glucose to HMF conversion using [EMIM]Br as the solvent [87]. All metal oxides showed reasonable activity in the formation of HMF at very low temperatures (60 °C) except Fe_2O_3 . However, their applicability is inconvenient since the product separation from the reaction liquor is difficult. Because of the low surface area of these metal oxides mesoporous metal oxides were used as catalyst. For example, the catalytic activity was reported for tungsten (W) doped ordered mesoporous oxides [88–90]. Introduction of early transition metals such as Nb and Ti enables to tune acidity and improve the production of HMF [89]. In addition, the introduction of Zr and vanadium (V) was investigated. However, it was revealed that doping these two metals did not improve catalytic activity [90]. Other mesoporous oxides tested include Ta [91,92], Nb [93], Ti [94], Zr phosphate [95,96], Sn phosphates [97] and Ta phosphates [98]. The reaction conditions, conversion rates and product yields over conventional supported catalysts are summarised and given in Table 3.

Table 3. Conventional supported catalysts, the conditions, and products in the conversion of biomass derived glucose to HMF.

Catalyst	T (°C)	Time (h)	Solvent	Glucose Conversion (%)	Product Yield (%)	Ref.
CrCl ₂ -Im-SBA-15	150	3	Phase 1: Water:DMSO (8:2 v/v) Phase 2: Butanol:MIBK (7:3 v/v) (Phase 1: Phase 2 = 1:1 v/v)	51	Selectivity: HMF: 69	[13]
CrCl ₂ -Im-SBA-15	150	3	Phase 1: Water Phase 2: MIBK (1:1 v/v)	67	HMF: 28	[12]
Nb-SBA-15	165	3	Phase 1: Water and NaCl Phase 2: THF	94	HMF: 62	[99]
AlNb/SBA-15	170	6	Phase 1: Water Phase 2: MIBK (1:2 v/v)	94	HMF: 56	[100]
Zr-MCM-41	175	2.5	Phase 1: Water Phase 2: MIBK	81	HMF: 23	[101]
Al-MCM-41	195	2.5	Phase 1: Water and NaCl (20 wt %) Phase 2: MIBK	98	HMF: 63	[102]
CeO ₂ -Sulfated-ZrO ₂ -SBA-15	120	6	iPrOH:DMSO (9:1 v/v)	90	HMF: 60	[103]
SAPO-34	170	0.7	Phase 1: Water Phase 2: γ -valerolactone	100	HMF: 94	[104]
Sn-Amberlyst-15	120	6	Phase 1: Water Phase 2: MIBK (1:1 v/v)	68	Selectivity: Fructose: 6 HMF: 15 Levulinic Acid: 45	[79]
Cr ³⁺ -Amberlyst-15	120	1	Phase 1: Water Phase 2: TEAB (1:9 w/w)	Not stated	HMF: 70	[80]
SCFC resin	120	1.5	DMSO	85	HMF: 8	[81]
PBnNH ₃ Cl	140	12	Phase 1: Water: DMSO (3:7 v/v) Phase 2: MIBK (Phase 1: Phase 2 = 1:4 v/v)	90	HMF: 45	[82]
Al ³⁺ -SPFR resin	180	1	Phase 1: Water Phase 2: γ -valerolactone	96	HMF: 42	[83]
Al ₇ Zr ₃	175	1	Phase 1: Water Phase 2: MIBK (1.5:3.5 v/v)	92	HMF: 46	[85]
Al ₂ O ₃	140	3	[EMIM]Br	96	HMF: 50	[86]

Table 3. Cont.

Catalyst	T (°C)	Time (h)	Solvent	Glucose Conversion (%)	Product Yield (%)	Ref.
NbWO ₃	120	1	Phase 1: Water Phase 2: THF (1:9 v/v)	90	HMF: 30 Fructose: 10	[89]
Nb ₇ W ₃ oxide	140	2	Phase 1: Water Phase 2: 2-Butanol (5:2 v/v)	100	Selectivity: HMF: 50	[93]
Ta ₇ W ₃	140	8	Phase 1: Water Phase 2: 2-Butanol	80	Selectivity: Fructose: 2 HMF: 47	[92]
SnP	175	1	Phase 1: Water and NaCl Phase 2: THF (1:3 v/v)	98	HMF: 61	[105]
MnPO ₄	160	1.5	Phase 1: Water Phase 2: THF	90	HMF: 59	[106]
Meso-TiWO ₃	120	1	Phase 1: Water Phase 2: THF (1:9 v/v)	70	HMF: 25	[90]
Meso-Ta ₂ O ₅	175	1.5	Phase 1: Water Phase 2: MIBK	69	HMF: 23	[91]
Meso-ZrP	155	6	Water	84	HMF: 47	[95]
Meso-SnP	150	0.3	Phase 1: Water Phase 2: MIBK (1:2 v/v)	50	HMF: 50	[97]
Meso-TaP	170	1	Phase 1: Water Phase 2: MIBK	56	HMF: 33	[98]
Al–Ti Sulfonated Carbon	130	5	DMSO	85	HMF: 57	[107]

Another promising support for the conversion of glucose into HMF is graphene oxide. The material itself contains carboxylic groups which facilitate the dehydration of fructose into HMF [108]. Furthermore, the conjugated structures of the graphene sheets promote interactions with reactants [109]. Zhang et al. [87] have investigated the effect of supporting Cr₂O₃, SnO₂, SrO and Fe₂O₃ on graphene oxide. Unexpectedly, Cr₂O₃, SnO₂, SrO decreased the activity towards HMF, whereas Fe₂O₃ increased the activity. It was stated that the activity of Cr₂O₃, SnO₂ and SrO in the glucose isomerization to fructose is inhibited due to the presence of –COOH groups on the surface of graphene oxide.

Wider pore silicas and amorphous silica alumina [110] have attracted the attention of researchers as alternative catalysts to zeolites and MOFs. The ordered mesoporous structure of these materials is expected to reduce the diffusion limitations and the ordered mesoporous silica have the advantages over its amorphous analogues the higher stability and well-defined acidity [111]. The MCM-41 is a widely studied ordered mesoporous silica. In order to prepare the material a surfactant, typically cetyl trimethyl ammonium bromide (CTAB), is mixed with a silicate precursors [112]. Simultaneously, a metal precursor can be introduced in the synthesis gel in situ to introduce metals or metal oxides to provide catalytically active sites. For instance, aluminium introduction into the synthesis gel mixture is reported in the literature widely to provide catalytic activity to MCM-41. In this synthesis procedure, micelles are formed by the surfactant molecules and the silicate and metal precursors form a polymeric network around the micelles. After the hydrothermal treatment, calcination removes the organic surfactant, the porous structure is retained by the

interconnected silica that forms the pores. The metal is dispersed either in oxide or metallic form on the surface or within the silica framework. Typically, the pores are cylindrical with a diameter in the range of 2–9 nm [112]. To improve activity of the porous silica for the glucose conversion to HMF, Zr [101] was introduced by using $ZrSO_4$ as precursor. Catalytic evaluation in the conversion of 10 wt% glucose mixture shows a conversion of over 80% and an HMF selectivity of 28% after 2.5 h reaction at 175 °C. Meanwhile, 47% fructose selectivity was obtained. Similarly, MCM-41 was used as the porous support where Al was introduced. The catalytic test in a biphasic H_2O -MIBK system with the addition of salt (NaCl), showed an HMF yield of 63% after 30 min [102]. Recycling experiments revealed only a small decrease in glucose conversion. An alternative mesoporous silica is SBA-15, which was studied as support for glucose conversion. The SBA-15 material differs from MCM-41 on the pore geometry. The SBA-15 structure is hexagonal, and the pore walls are thicker which makes it slightly more stable than MCM-41. Zr sulphates were supported on SBA-15 for the conversion of glucose to HMF [103]. These active sites, namely sulphated zirconia, introduces a well-known strong acid character to the SBA-15 silica support [113,114]. Over these materials, the conversion of glucose in DMSO led to an HMF yield of 66%. In a radical approach, Degirmenci et al. showed that the homogenous catalytic reaction system of the $CrCl_2$ -ionic liquid could be created on the surface of SBA-15. This has the advantage to replicate the active homogeneous coordination environment for the conversion of glucose and retains the advantages of using a heterogeneous catalyst. Furthermore, the ionic liquid could be replaced with a greener and cheaper solvents such as water. In this approach, the ionic liquid was grafted onto the walls of SBA-15 and the metal salt $CrCl_2$ was coordinated on the surface with the ionic liquid [13]. Although it is promising, the mesoporous silica materials are prone to hydration and their stability in aqueous solutions is limited. Therefore, organic solvents such as DMSO need to be used and thus their utilisation as catalyst supports for glucose conversion is not feasible. Further developments are needed to improve their hydrothermal stability for an efficient catalytic system.

6. Conclusions and Outlook

Biomass feedstock can be utilised through carbohydrate conversion into HMF. Catalysts play a pivotal role in adding value to this widely available and cheap resource and pave the way to a renewable based green chemical industry. Heterogeneous catalysts are crucial to realise a large-scale application. However, hydrothermal environment during the transformation of biomass-based sugars into HMF puts heterogeneous catalysts under test for their poor hydrothermal stability. The organic additives and biphasic systems are shown to improve the product yield but meanwhile this would sacrifice the green nature of a simple conversion process in water with a recoverable heterogeneous catalyst. However, it has not been possible to achieve high product selectivity or long-term stability under these simple conditions. Therefore, the trade-off lies between finding a catalyst to deliver high product yield and keeping the engineering of the system simpler and greener.

Novel catalysts have been explored by the researchers, and the challenges remain (Table 4). Recent significant breakthroughs in the field include, but are not limited to the enhanced understanding of the reaction mechanism on the conversion of glucose in homogeneous and heterogeneous systems, particularly over Sn-Beta. A novel approach involving MOFs has shown how to exploit their simple synthesis protocols and provide fine-tuning of their structure and thus their catalytic properties. Amongst all the catalytic systems reviewed, catalysts with dual acid functionality seems promising. Lewis acidity for glucose isomerisation and Brønsted acidity for subsequent dehydration to HMF in a single stage, one-pot conversion to HMF remains desirable. The long-term stability of catalysts is of great interest. Therefore, the investigation of new catalysts under continuous flow will be informative in terms of their potential for commercial large-scale applications.

Table 4. Summary of the advantages and disadvantages of the classes of heterogeneous catalysts used in glucose conversion to HMF.

Catalysts	Pros and Cons
Zeolites	<ul style="list-style-type: none"> ■ Commercially available, industrial uptake is quick. ■ Easy to reactivate by calcination to remove humin deposits. ■ Well defined crystal structure allows generation of uniform active sites. ■ Stable at elevated temperatures and in solvents. ■ Synthesis requires harsh chemicals and elevated temperatures and pressures. ■ Deactivates fast in liquid phase glucose conversion reaction conditions.
MOFs	<ul style="list-style-type: none"> ■ Functional groups can easily be introduced. ■ The porosity of the framework can easily be altered by using different metal ions and functional linkers. ■ Stability in water, greenest solvent is limited. ■ Catalyst recycling and removal of humin deposits cannot be achieved by easy re-calcination.
Conventional Supported Catalysts	<ul style="list-style-type: none"> ■ Readily available supports make them easy to implement. ■ Easy to reactivate by heat treatment at high temperatures. ■ Stable in various solvents, and high temperatures, and pressures. ■ Functionalization of them does not lead to uniform active sites. ■ Their porosity is limited. ■ Glucose conversion and product selectivity are usually lower than MOFs and zeolites.

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