Recent catalytic advances in the chemistry of substituted furans from carbohydrates and in the ensuing polymers

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In this review, an overview is given on the last development of catalytic methods for the preparation of substituted furans from carbohydrates and ensuing polymers. The review starts with the recent aspects in the synthesis of some key furan monomers in the presence of solid catalysts. In the second part, selected examples are given of polymerization systems leading to furan-based materials with promising properties, thus constituting a serious alternative to petroleum-based counterparts. Finally, a short examination is given on what could be the future of furan chemistry with the recent development of ionic liquids as solvents.

KEY WORDS: carbohydrates; catalysis; furanic monomers; furanic polymers.

1. Introduction

The growing interest for the preparation of non-petroleum chemicals has naturally led to the development of the nonfood transformation of carbohydrates, the most abundant source of renewable materials on earth, into valuable chemicals [1]. This renewed interest was quite obvious with the development of the chemistry of furanic compounds, particularly for the preparation of nonpetroleum-derived polymeric materials such as polyesters, polyamides and polyurethanes [2,3].

Two basic nonpetroleum chemicals readily accessible from renewable resources, furfural (2-furancarboxalde-hyde, (**1**)) arising from the acid-catalyzed dehydration of pentoses, and 5-hydroxymethylfurfural (5-hydroxy-methyl-2-furancarboxaldehyde (**2**)) arising from the acid-catalyzed dehydration of hexoses, are suitable starting materials for the preparation of further mono-mers required for polymer applications. Whereas the former is industrially available (200 000 tons/year), the latter was only produced on a pilot plant scale [4]. However, in spite of the high potential of furanic intermediates derived from (**2**), this basic disubstituted furan is not yet produced on industrial scale, as the present politico-economical situation still favors the petroleum route. The general strategy representing the approach of furanic first-generation monomers (**1** and **2**) is sketched in scheme 1.

5-Hydroxymethylfurfural (**2**) has been used for the manufacture of phenolic resins by reaction of the aldehyde group as well as of the hydroxymethyl group [1]. However, high potential organic intermediate

chemicals are the various ensuing products of (**2**) as partially illustrated in scheme 2. 2,5-Disubstituted furan derivatives are particularly suitable as they can replace their corresponding aromatic counterparts [5,6]. For example, as it will be seen in the second part of this review, 2,5-furandicarboxylic acid (**7**) is capable of replacing terephthalic or isophthalic acids for the preparation of polyesters, polyamides and polyur-ethanes. 2,5-Furandicarboxaldehyde (**6**) is a starting material for the preparation of 2,5-bis(aminomethyl)-furan and also for the preparation of Schiff bases. 2,5-Bis(hydroxymethyl)-furan (**4**) is already used in the manufacture of polyurethane foams [7]. The fully saturated 2,5-bis(hydroxymethyl)-tetrahydrofuran (**5**) can be used as a diol in the preparation of polyesters. Finally, the new compound 2-hydroxymethyl-5-vinyl-furan (**8**) can be a starting material for the preparation of epoxy resins.

5-Hydroxymethylfurfural has also been identified as a novel scaffold for the generation of disubstituted furan derivatives, an important component of pharmacologi-cally active compounds, which are associated with a wide spectrum of biological activities [8].

Several attempts have since been made to develop new catalytic low-cost processes, more performant, more selective and environmentally safe, for the transformation of fructose and fructose precursors into 5-hydroxymethylfurfural and 2,5-disubstituted furans. This review will summarize the last developments in this field with emphasis on the preparation of some key intermediates, as illustrated in scheme 2, and their use in the preparation of polymeric materials.

As reported in a previous paper [9], a considerable interest has emerged these last thirty years for the application of solid heterogeneous catalysts in fields
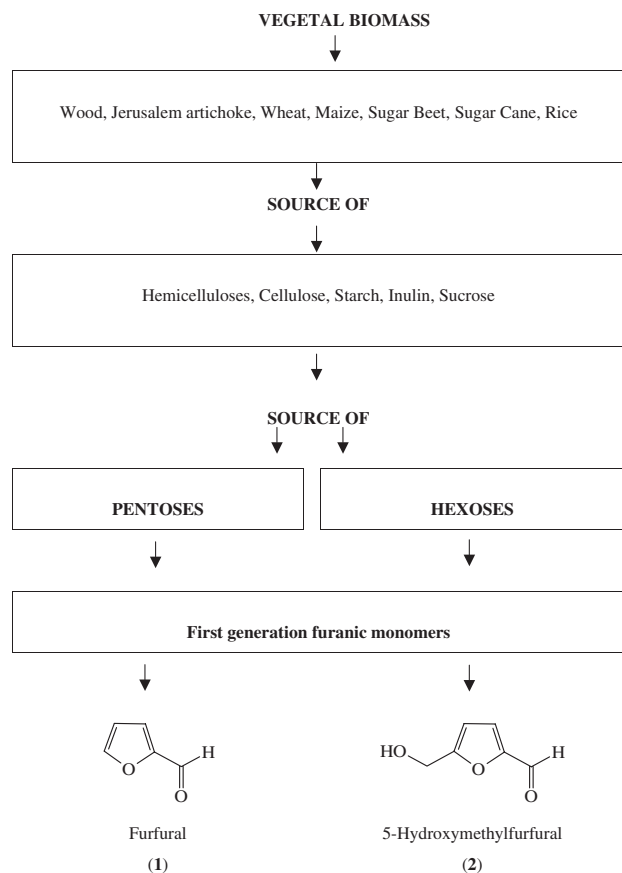
Scheme 1. From vegetal biomass to furfural (**1**) and hydroxymethylfurfural (**2**), the two first-generation furanic monomers.
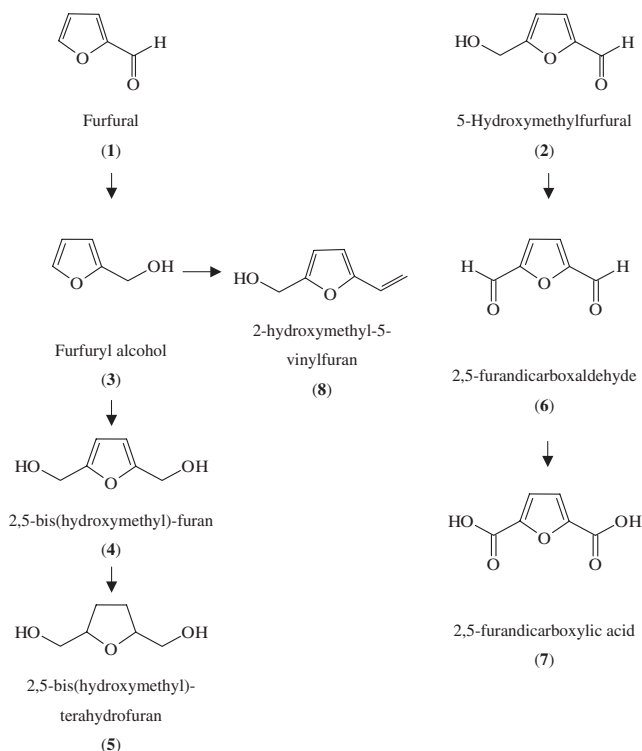
Scheme 2. Some of key furan derivatives.

other than oil refining and petrochemistry. Indeed, zeolites and related materials can be used as highly selective and active catalysts in the synthesis of bulk and fine chemicals [10–17]. Furthermore, their acidic and basic properties, as well as their hydrophilic and hydrophobic properties, can be combined with the structural properties of these materials in order to take advantage of their sorption and shape selectivity properties, the latter being an advantageous feature of zeolites compared to other heterogeneous catalysts.

2. Part I: Furan-based monomers

2.1. 5-Hydroxymethylfurfural

The most convenient method for the preparation of 5-hydroxymethylfurfural is the acid-catalyzed dehydration of fructose (scheme 3).

A review by Lewkowski on the chemistry of 5-hydroxymethylfurfural (**2**) and its derivatives has recently appeared [18], but is unfortunately far from being updated. Apart from the reviews by Gaset [19,20], the two more recent and exhaustive reviews are those by Kuster [21] and Descotes [22].

Two basic articles by Kuster [23] and van Bekkum [24] report an exhaustive study of all the parameters capable of influencing the course of the homogeneously catalyzed dehydration of fructose in water as the most convenient solvent. Whatever the operating conditions, the highest selectivity in (**2**) (75%) was obtained in the presence of methyl isobutyl ketone as simultaneous extraction solvent. In another work, the introduction of vapor extraction of (**2**) yields a product with a high purity, but to the detriment of the yield [25].

When acidic ion-exchange resins are used in water in place of mineral acids, some improvements are obtained in terms of process due to the presence of solid catalysts, but the selectivity in 5-hydroxymethylfurfural is not significantly improved [26–28].

However, in the literature, the highest selectivities in 5-hydroxymethylfurfural (**2**) have been obtained in DMSO as the solvent under moderate operating conditions. Fructose is selectively and quantitatively converted into (**2**) in the absence of catalyst as well as in the presence of ion-exchange resins [29–32]. The advantage of using DMSO as solvent is that this dipolar
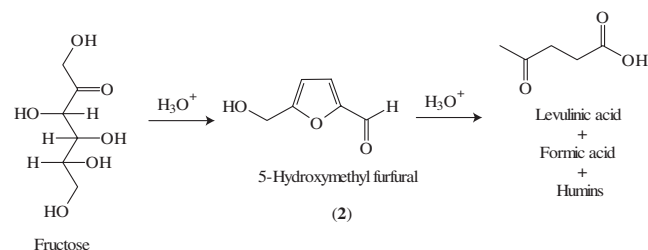
Scheme 3. Simplified reaction scheme for the dehydration of fructose.

aprotic solvent prevents the formation of levulinic acid and humins as well, but the corresponding disadvantage is concerned with the separation of DMSO, (2) and water formed, and also with some possible toxic S-containing by-products arising from the decomposition of DMSO.

Taking into account the results reported in the recent literature on the dehydration of fructose into (2), in particular, those dealing with the use of strongly acidic ion-exchange resins, it was expected that the low selectivity to 5-hydroxymethylfurfural (2) observed in water as solvent could result from the presence of hydronium species within the macropores of the resins, leading to its further degradation [9]. It was then postulated that microporous zeolitic materials as catalysts could lead to improvements in the dehydration reaction, mainly due to the possible tuning of their acidic and basic properties, their hydrophilic and hydrophobic properties, and their adsorption and shape selectivity properties, the latter being an advantageous feature of zeolites compared to other heterogeneous catalysts [9].

Fructose dehydration was then performed in the presence of microporous catalysts, namely, dealuminated H-form zeolites in a water/methyl isobutyl ketone (1/5 by volume) mixture [33–35]. A mordenite in the protonic form, with a Si/Al ratio of 11 and a low mesoporous volume, was found to offer the best balance between activity, selectivity and by-product amounts at 165 °C. A selectivity in 5-hydroxymethylfurfural (2) of 91–92% was obtained up to a fructose conversion of 76%. However, in most other cases, the selectivity tends to decrease by increasing the Si/Al ratio, i.e., by increasing the acidity of the catalytic sites, thus allowing secondary reactions to take place, such as the formation of formic and levulinic acid or polymeric materials referred to as humins. Compared to other catalytic systems, the structure of mordenite with only parallel large elliptical channels will allow the accessibility of fructose to the catalytic sites and the rapid diffusion of (2) once formed, while avoiding its rearrangement into higher molecular weight compounds.

A pilot plant using a new solid–liquid–liquid reactor, resulting from the modification of a liquid–liquid extraction pulsed column, was then developed [36]. 5-Hydroxymethylfurfural (2) is extracted continuously with methyl isobutyl ketone in a countercurrent manner with respect to the aqueous fructose phase and catalyst feed. In such a process, the residence time of the intermediate in the aqueous phase is shortened, and the consequence was a gain in selectivity of about 10%.

From an economical point of view, it was more interesting to start from raw fructose-containing precursors such as sucrose and inulin hydrolysates instead of fructose itself. In the presence of the H-mordenite (Si/Al = 11), selectivities to 5-hydroxymethylfurfural between 92 and 97% for fructose conversions up to 54%

at 165 °C have been obtained [34]. Under the operating conditions used, glucose does not react significantly and is only acting as a spectator in the dehydration step. The production of (2) from fructose-containing precursors is then a more interesting and economical route, as the unreacted glucose can be easily separated from the reaction medium in a liquid–liquid extractor working in a countercurrent mode.

It must also be mentioned that fructose can be obtained from fructose precursors such as sucrose and inulin by catalytic heterogeneous processes using zeolitic materials instead of processes using mineral acids, ion-exchange resins or enzymes. It was shown that hydrolysis of those precursors into glucose and fructose was selectively achieved over zeolites in their acidic form [37]. Glucose and fructose can be separated over zeolites in their cationic form [38,39]. In a similar manner, hydrolysis of glucose precursors such as starch, maltose and cellobiose has also been easily achieved over acidic zeolites. It was also shown that the selective isomerization of glucose into fructose was working over cation-exchange zeolites [40,41] and hydrotalcites [42]. In the latter case, a very high selectivity in fructose is obtained, but at a glucose conversion close to 20% only. It should also be added that hydrotalcites are easily regenerated, whereas, in the case of cation-exchange zeolites, some lixiviation phenomenon can occur. Such an approach may also be advantageously used in food applications for the preparation of invert sugars since zeolitic materials are known for their catalytic as well as for their sorption properties and are more easily recycled than ion-exchange resins [43,44].

As far as the fructose route to 5-hydroxymethylfurfural (2) is not yet developed on an industrial scale, another route to obtain 2 was to start from a cheap and readily available starting material such as 1a (scheme 4). This route involves hydroxymethylation of furfural (1a) with formaldehyde.

Hydroxyalkylation of aromatics and heteroaromatics was recently shown to fail in the presence of aldehydes or epoxides as hydroxyalkylating agents and H-form zeolites as catalysts [45–47]. However, one reference mentioned traces of 5-hydroxymethylfurfural (2) when furfural (1a) is reacted together with aqueous formaldehyde in the presence of sulfonic ion-exchange resins [48]. After several attempts to determine the most
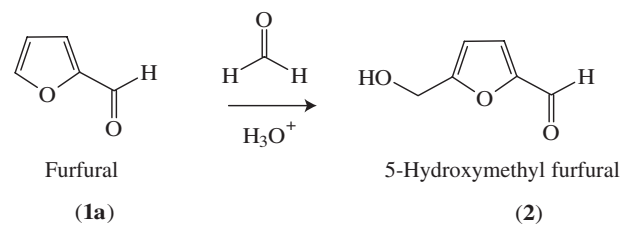
Scheme 4. Simplified reaction scheme for hydroxymethylation of furfural.

appropriate operating conditions to be used, solvent, source of formaldehyde and catalyst, it was found that the reaction could work with a large excess of aqueous formaldehyde in the presence of dealuminated H-mordenites at low temperatures [49]. However, the selectivity in (2) was relatively poor, around 30%, whatever be the acidic and hydrophobic properties of the catalyst. A slight increase in the selectivity to 5-hydroxymethylfurfural (2) was observed with toluene as the solvent, up to 50%, but at a low furfural conversion. In fact, the low selectivity results from the deactivation of the electron-withdrawing aldehyde group on the C-5 carbon position. Owing to this deactivation effect, the principal reaction is the addition of formaldehyde to the aldehyde group of furfural leading to aldolized, croto-nized and heavier molecular weight compounds referred to as resins. When the electron demand of the substituent is reversed as, for example, by protecting the electron-withdrawing aldehyde function with an electron-donating 1.3-dithiolane function (scheme 5), the selectivity to the corresponding hydroxymethylated derivative easily reaches 90% [50].

It is also worth mentioning that zeolitic materials have been successfully used in the dehydration of xylose and precursors to furfural [51]. Furfural is obtained through dehydration of pentoses, xylose in particular, or hemicelluloses, at high temperatures (200–250 °C), and in the presence of mineral acids as catalysts, mainly sulfuric acid [52]. Under these conditions, the selectivity in furfural does not exceed 70%, except in the case of its continuous extraction with supercritical CO_2, where it reaches 80% [53].

In the presence of zeolites as catalysts, a close parallelism is observed with the results obtained for the dehydration of fructose over the same catalysts, except that toluene is the cosolvent instead of methyl isobutyl ketone. The transformation of xylose into furfural is easily achieved at 170 °C with a selectivity as high as 90–95%, as long as the conversion is kept low, i.e., 30–40%. At those high temperatures, ion-exchange resins cannot compete with zeolites. Nevertheless, it should be mentioned in the case of xylose dehydration that the formation of heavy compounds is less probable compared to what occurs in fructose dehydration to 5-hydroxymethylfurfural (2), which can react through its hydroxymethyl function, thus yielding higher molecular weight compounds.

Although one zeolite of the faujasite family was already checked several years ago in the dehydration of fructose, but with the formation of traces only of (2) [54], it is now clear that zeolitic materials with adequate structures and well-controlled properties could replace the catalytic systems used up to now.

However, new catalytic systems have also been developed by other research groups during the last decade. Nb-based catalysts were used in the dehydration of fructose with high catalytic efficiency, at only 100 °C,
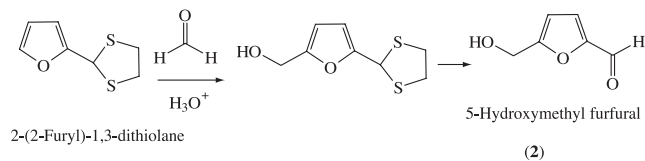
Scheme 5. Selective route to 5-hydroxymethylfurfural after protection and deprotection steps.

in water and without any extraction solvent. A high selectivity in 5-hydroxymethylfurfural (2), 70–80%, at a fructose conversion of 30–50%, has been reported [55]. A more complete work over niobium oxide, H_3PO_4-treated niobic acid and niobium phosphates treated at different temperatures, was published later [56] and has confirmed the previous results, i.e., the reactions work at low temperature (100 °C), and high selectivities in 5-hydroxymethylfurfural, up to 100% as determined by GC-MS analysis, are obtained, but at low fructose conversion, 25–30%, and relatively short reaction times, about 0.5–1 h. A nearly similar approach was also carried out in the presence of Zr- and Ti-based catalysts with different structural forms [57]. Once again, excellent results are reported. Selectivities in (2) as high as 100% are reported over cubic zirconium pyropho-sphate and γ-titanium phosphate catalysts, at reaction times and fructose conversion of the same order of magnitude as those reported for Nb-based catalysts.

Other recent articles by Ishida report the catalytic dehydration of fructose and glucose in the presence of lanthanide(III) salts. At 100 °C in organic solvents, namely DMSO, dimethylformamide (DMF) and DMA, the yields in 5-hydroxymethylfurfural (2) are over 90% after a reaction time of 4 h in the presence of $LaCl_3$ [58]. As already reported in the literature, DMSO was found to be the best solvent that prevents the formation of levulinic acid and other by-products. In water at 140 °C, both fructose and glucose are smoothly dehydrated into (2) with selectivities higher than 95%, but only around 10% of conversion at 15 min is obtained in the initial stages of the reaction [59]. As reported by the authors, the material balance gradually decreases after 20 min, and the ultimate product yield of ca. 40% is obtained after 120 min, whatever be the starting quantity of hexose, fructose or glucose.

Two very recent papers are also worth noting: (i) The first one [60] takes into account the fact that high selectivities in 5-hydroxymethylfurfural are often obtained in high boiling polar solvents, leading to expensive separation procedures, and examines the dehydration of fructose, glucose, sucrose and inulin in a sub- and supercritical mixture of acetone and water. Contrary to the reaction performed in supercritical water [61], no solids (humic acids) were produced. Under optimized operating conditions in acetone/water mix-tures, 10 g/L of fructose, 10 mmol/L of H_2SO_4, 180 °C and 20 MPa, both selectivity in 5-hydroxymethylfurfural

and fructose conversion increase with decreasing water content. A nearly complete fructose conversion is attained within 2 min in the solvent mixture containing 90 v/v% of acetone. Also remarkable are the selectivities in 5-hydroxymethylfurfural (yields at 100% starting material conversion) obtained—77% from fructose, 78% from inulin, 48% from glucose and 56% from sucrose—which led the authors to propose, from their new technical process, an acceptable price of about 2 €/kg for 5-hydroxymethylfurfural if fructose, or fructose-rich precursors, are available at a price of 0.5 €/kg; (ii) The second one, by Ribeiro and Schuchardt [62], who have investigated the catalytic one-pot cyclization and oxidation of fructose over bifunctional and redox catalysts, namely, cobalt acetylacetonate encapsulated in sol–gel silica. Although the clear objective was the preparation of 2,5-furandicarboxylic acid, it was shown that, at 165 °C and under a 2 MPa air pressure, fructose is selectively converted into 5-hydroxymethylfurfural within 1 h and a fructose conversion close to 50% over a SiO$_2$ gel catalyst.
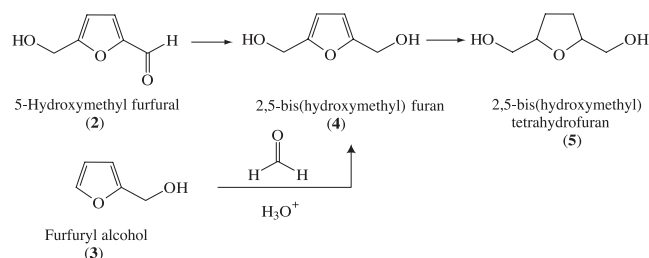
2.2. 2,5-Bis(hydroxymethyl)-furan

As already mentioned, 2,5-bis(hydroxymethyl)-furan (4) is used in the manufacture of polyurethane foams [7], and its fully saturated form (5) can be used as a diol in the preparation of polyesters. The market for this latter compound would be 8000 tons per year at a price of around 7 €/kg [63].

The two catalytic routes to (4) developed up to now are the hexose route through hydrogenation of 5-hydroxymethylfurfural and the pentose route through hydroxymethylation of furfuryl alcohol (3) (scheme 6).

2.2.1. Hydrogenation of 5-hydroxymethylfurfural

Hydrogenation of 5-hydroxymethylfurfural (2) has been studied in an exhaustive manner by Descotes et al. [64]. The initial strategy was based on the assumption that the hydrogenation of (2) would be more rapid than the dehydration of fructose, thus avoiding the formation of secondary products by trapping (2) once formed. Unfortunately, the experimental results were not those that were expected.

Hydrogenation of 5-hydroxymethylfurfural was then performed under conventional operating conditions of temperature and pressure and over conventional hydrogenation catalysts, Raney nickel, copper chromites and C-supported metals. Nearly quantitative yields in (4) and/or 2,5-bis(hydroxymethyl)-tetrahydrofuran (5) have been obtained in water as the solvent, in relatively short reaction times, at 140 °C and 70 bar of hydrogen. Hydrogenation of the aldehyde group of (2) and saturation of the furan ring may occur in the presence of most of the catalysts used, but a careful control of the experimental conditions also allows to stop selectively at the 2,5-bis(hydroxymethyl)-furan stage.

Most of the recent works on hydrogenation of furan derivatives were mainly concerned with the improvement of catalytic systems to perform hydrogenation of furfural into (3), which is still industrially using copper chromites as catalysts. Copper chromites are effectively known to selectively hydrogenate the carbonyl function while leaving the C–C double bond unchanged. They are also known to deactivate relatively rapidly in the absence of stabilizing species [65]. Moreover, new environmental constraints prevent Cr-containing catalysts from being used in the future, and this led to the development of new C-based catalytic systems. Copper dispersed on activated carbon catalyst was shown to display a higher activity when reduced at 300 °C than at 400 °C and a selectivity to furfuryl alcohol comparable to that obtained with copper chromite catalysts in the vapor-phase hydrogenation of furfural [66]. Also worth noting is the absence of deactivation for 10 h onstream.

Raney nickel catalysts are known for their absence of selectivity in the hydrogenation of furfural into furfuryl alcohol. Hydrogenation of the carbonyl bond competes with ring saturation into tetrahydrofurfural and further hydrogenation of the aldehyde group to yield tetrahydrofurfuryl alcohol. However, in the liquid-phase hydrogenation of furfural, it was recently reported that Raney nickel catalysts modified with heteropolyacid salts achieve hydrogenation of furfural into furfuryl alcohol with a selectivity in alcohol as high as 98.1% at a furfural conversion of 98.5%, at 80 °C in ethanol as solvent and 20 bar of hydrogen [67].

2.2.2. Hydroxymethylation of furfuryl alcohol

In the preparation of 2,5-bis(hydroxymethyl)-furan resins (4) used as active and fast-curing foundry binders [7], the first step is the addition of formaldehyde to furfuryl alcohol (3) in the presence of acetic acid as solvent and catalyst, followed by further polymerization with the starting alcohol to produce resins with the desired properties (scheme 6).

In the presence of solid catalysts such as ion-exchange resins, it was shown that it was possible to stop at the monomer stage, but with a 28% yield after 120 h of reaction [68].

However, it has been shown that protonic zeolites with controlled structure and acidity were capable of performing hydroxymethylation of furfural into

5-Hydroxymethyl furfural
(2)

2,5-bis(hydroxymethyl) furan
(4)

2,5-bis(hydroxymethyl) tetrahydrofuran
(5)

Furfuryl alcohol
(3)

Scheme 6. Routes to 2,5-bis(hydroxymethyl)-furan.

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