Zeolites as efficient catalysts for key transformations in carbohydrate chemistry

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ARTICLE INFO

ABSTRACT

Acid zeolites as catalysts offer unique achievements in the carbohydrate field allowing regio- and stereocontrolled reactions, mainly related to their shape-selective properties. Moreover, these materials are environmentally safe and easy to handle, contributing to clean and sustainable procedures in carbohydrate transformations. The scope of this review is to summarize the most significant applications of these heterogeneous catalysts in carbohydrate chemistry, notably in mediating key transformations such as glycosylation, sugar protection and deprotection, hydrolysis and dehydration, highlighting the exciting results that the use of zeolites may provide.

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1. Introduction

Many transformations in carbohydrate chemistry require acid catalysis and zeolites, as heterogeneous catalysts, can serve as an environmental friendly alternative to the traditional chemical synthetic routes. The range of well-defined zeolites available, and their advantages as easily recovered, and reusable materials, has prompted to their application, contributing to green and sustainable procedures for the conversion of carbohydrates. Furthermore, the shape-selective properties of zeolites, which can be used to avoid the formation of undesired products, allow stereo- and regioselective reactions, a challenge for the transformation of multifunctional molecules such as carbohydrates.

In the last few years major advances have been described addressing the use of zeolites as promoters in classical and key steps for the derivatisation of sugars. The present review summarizes the results reported on the reactions promoted mainly by acid zeolites in the carbohydrate field, covering both early work and recent developments in this area.

2. Overview of the use of zeolites in organic synthesis

It is not our intention to cover structural aspects of zeolites and their applications in organic chemistry, as a number of excellent reviews and books have already been published [1,2]. Instead, in this section, we emphasize the reasons which make them of interest in organic synthesis. These microporous crystalline materials, which possess a characteristic aluminosilicate framework, arranged by $[SiO_4]$ and $[AlO_4]^-$ tetrahedra that are linked by oxygen bridges, have been widely used as environmentally safe catalysts in the synthesis of organic compounds.

There are several characteristics that make zeolites unique materials among other solid catalysts. Their regular size cavities, i.e. pore apertures, channels and cages, whose dimensions can fit molecule shape, may provide selectivity for reactants, products and transition states. That allows only molecules of appropriate dimensions to enter the zeolite cavity, to diffuse through the pores, with the stabilisation of one transition state over another. Size restrictions inside the zeolite cavities may also contribute to the stereo- and regiocontrol of some organic transformations performed over these materials. Other important feature is their adsorption properties, which enable reactants to be differently or preferentially adsorbed onto the zeolite. However, one of the major issues from the environmental point of view is that zeolites possess both Brønsted and Lewis acidity, replacing and avoiding thus the use of less environmentally acceptable acid catalysts such as $AlCl_3$, H_2SO_4, in organic transformations. Their acidity can be modulated by changing the aluminosilicate framework, and a vast range of zeolites with different acid strengths are known.

From the main zeolite-mediated organic reactions we can underline the electrophilic aromatic substitution, namely Friedel–Crafts alkylation or acylation [3a,b], processes that have been used for the synthesis of important intermediate organic compounds. An elucidative example is the regioselective *p*-acylation of toluene with acetic anhydride over HBEA zeolites, which affords *p*-methylacetophenone in nearly quantitative yield [3b]. The Mobil-Badger process [4], used for the production of ethylbenzene from benzene and ethylene, is a typical zeolite-catalysed Friedel–Crafts alkylation, providing the precursor for styrene (and hence polystyrene) manufacture.

Zeolites have been described as efficient catalysts for benzyl ether deprotection [5], acetal hydrolysis [6], stereoselective dehydration of aliphatic, aromatic, and heteroaromatic 2-hydroxy-

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nitroalcohols to give only (*E*)-nitroolefines [7] and for the transesterification of β-keto esters with a variety of alcohols [8], to cite a few examples of their useful applications.

Moreover, zeolites proved to be valuable catalysts of a number of isomerisations and skeletal rearrangements. The isomerisation of xylenes and butenes and the Beckmann rearrangement of ketoximes to lactams [9] are two important industrial processes in which zeolites have been employed. Other acid-catalysed reactions such as the Fries rearrangement of phenyl esters to *o*- and *p*-acylphenols [10], the Claisen rearrangement of allyl aryl ethers [11] and the rearrangement of epoxides to aldehydes or ketones [12] have been performed with zeolites.

There are several reactions in carbohydrate chemistry which require acid catalysts such as most of the *O*-glycosylation methods or the synthesis of sugar acetals, namely *O*-isopropylidene derivatives and their cleavage. Zeolites have been employed as mild alternative heterogeneous acid catalysts for some of these transformations. In the following sections, we will focus on the most significant of these approaches.

3. Zeolites in carbohydrate chemistry

Separation of carbohydrates using zeolites has been developed by Wortel and van Bekkum [13] and Buttersack et al. [14a] and these materials continue to be very helpful for the purpose [14b]. Zeolites were employed to produce fine chemicals from carbohydrates in 1994 [15] and first reported to mediate transformations in carbohydrate chemistry in 1995 [16]. In 2002 Moreau revised the use of zeolites for food and non-food transformations of carbohydrates [17]. We now focus on the main zeolite-catalysed approaches and include the latest findings in the field.

3.1. Glycosylation

The first glycosylation reaction was reported more than a hundred years ago by Fischer [18]. It involves the direct mineral acid-catalysed acetalation of a sugar with an alcohol. This procedure has become a mainstay of carbohydrate chemistry. Meanwhile several approaches have been developed for the synthesis of glycosides, namely with the use of Lewis acid catalysts. Due to the biological significance of glycoconjugates, glycoside synthesis became a main area of research and was previously reviewed [19].

In 1996 Corma et al. [20a] reported the preparation of butyl glycosides in very good yield by Fischer glycosylation using zeolites as catalysts and avoiding the main draw back of this reaction, which is the formation of oligomeric species. Kinetic experiments indicated that the catalytic activity relied on the zeolites Brønsted acid sites and confirmed that the mechanism is identical to that commonly accepted for Fischer type glycosylation, that is formation of an open chain hemiacetal followed by nucleophilic cyclisation from the C-4 hydroxyl group resulting in the kinetic glucofuranosides (**2a,b**) followed by a slow ring expansion to the corresponding butyl glucopyranosides (**3a,b**) (Scheme 1). Different zeolites were screened in order to find out the most appropriate one with respect to activity and selectivity. When increasing the amount of H⁺ in NaHY zeolites, their activity increased exponentially indicating that not all acidic sites are equally active for the Fischer glycosylation of D-glucose, but mainly those with medium and high acidic strength. Zeolites with different topologies were also investigated for the same reaction, namely modernite, HY-100, H-Beta and ZSM-5, and the best results were achieved using the large pore tridimensional H-Beta zeolite. Moreover, the crystal size and Si/Al ratio of the latter zeolite were shown to affect reactivity and selectivity of this reaction [20b]. Crystallite size equal or below 0.35 μm proved to give the maximum effectivity, while a higher selectivity for the

furanoside form was found by increasing this parameter above 0.35 μm.

The same group [21] investigated the direct transacetalation of the previously described mixture of butyl glucofuranosides (**2a,b**) and glucopyranosides (**3a,b**) by reaction with octanol or dodecanol in the presence of H-Beta zeolite. Parameters such as temperature, molar ratio of the reactants, Si/Al ratio and consequently hydrophilic character of the zeolite were evaluated. Moreover, the direct reaction of D-glucose with long-chain alcohols was successfully achieved suggesting a possibility for the commercial application of zeolites in the preparation of long-chain alkyl glucosides particularly interesting as non-ionic surfactants for cosmetics, food emulsifiers and detergents [22].

Chapat et al. [23] reported the synthesis of butyl D-glucosides over dealuminated HY faujasites by acetalation of D-glucose with *n*-butanol. The time dependence of the products concentration showed that butyl D-glucofuranosides are the kinetic products of the reaction, which concentration decreases with time to give the thermodynamically more stable butyl D-glucopyranosides in agreement with the results of Corma et al. [20a].

O-Glucosylation of 1,2-anhydro sugars in the presence of cyclohexanol was achieved using different zeolites such as HM, HY and NaY. Zeolite HY with an intermediate acidity proved to be the most effective catalyst, resulting exclusively in the desired β-glucoside in 79% yield [24].

Our group reported the first Fischer-type glycosylation of *N*-acetyl-α-D-galactosamine (GalNAc) with methanol catalysed by zeolites [25]. The large and medium pore zeolites HY, HZSM-5 and HBEA were investigated and zeolite HY (Si/Al ratio 3.1) was the most efficient catalyst, leading to the highest yield of methyl β-galactofuranoside (**4**), isolated as its acetylated (**5**) or isopropylidene (**6**) derivatives (Scheme 2). The results indicate that with large pore zeolites, the reaction efficiency depends upon the concentration of the zeolite acid sites and its hydrophilicity. However, the best regioselectivity for β-galactofuranoside versus β-galactopyranoside was obtained with the medium pore zeolite HZSM-5, which also led to the optimal conversion, suggesting that both the zeolite pore size and topology are determinant for this reaction.

Preparation of fully acetylated aryl glycosides using sugar peracetates as donors and Lewis/Brønsted acids as catalysts was first reported by Helferich and Schmitz-Hillebrecht in 1933 [26]. Aryl glycosides find applications as chromogenic substrates for glycosidases [27] as well as inhibitors of carbohydrate–lectin interactions [28]. Zeolites, namely H-Beta zeolite, were first used as catalysts for sugar per-*O*-acetylation by Bhaskar et al. [29] and the latter proved to be highly efficient, probably due to its greater acid strength and larger pore size, as well to its channel intersections. Therefore, Aich and Loganathan [30] tested the feasibility of H-Beta zeolite-catalysed Helferich glycosylation using β-D-glucose and β-D-galactose pentaacetates as donors and a variety of phenols as acceptors. Aryl 2,3,4,6-tetra-*O*-acetyl-β-D-glycopyranosides were obtained in reasonable yield ranging from 36% to 46% together with the corresponding aryl 3,4,6-tri-*O*-acetyl-α-D-glycopyranosides. These Helferich-type glycosylation by-products were obtained in 23–28% yield, quite a good yield when compared to that obtained by multi-step methodologies which give a maximum overall yield of 12% for the same type of compounds. These partially protected products are of interest for the synthesis of 2-deoxy, 2-azido and 2-deoxy-2-halo glycosides. Moreover, the same authors reported recently [31] the use of different forms of Beta-zeolites (H-Beta, Na-Beta, Fe-Beta and Zn-Beta) as catalysts for the synthesis of several long-chain alkyl glycopyranosides under solvent free conditions. Hence, glycosylation of penta-*O*-acetyl-β-D-galacto- and glucopyranoses with cetyl, dodecyl, octyl and 2-ethylhexyl alcohols afforded the alkyl 2,3,4,6-tetra-*O*-acetyl-β-D-pyranosides as major
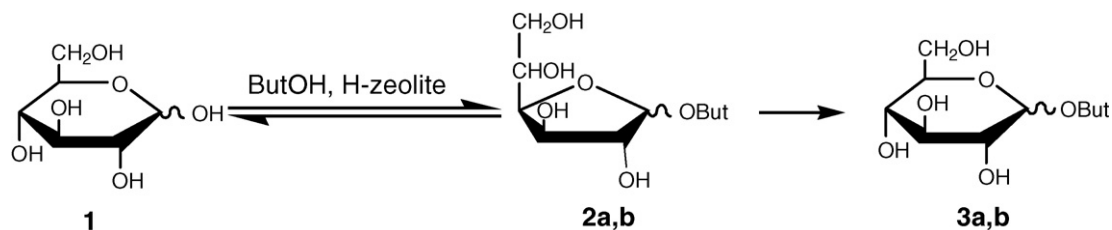
Scheme 1. Formation of butyl glycosides by acid zeolite-catalysed Fischer glycosylation.
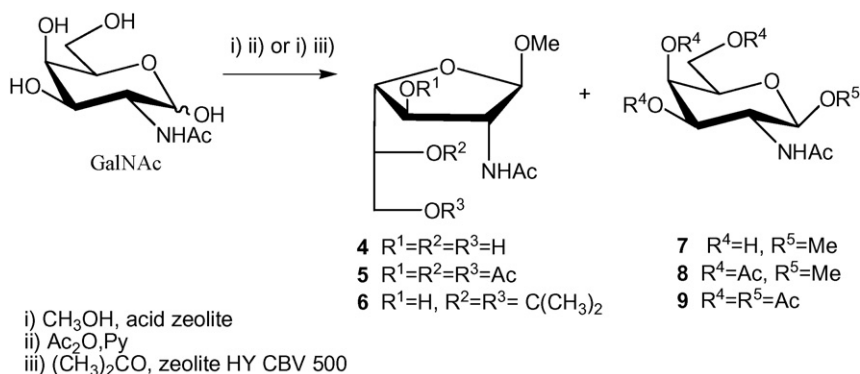
Scheme 2. Fischer glycosylation of GalNAc mediated by acid zeolites.

products and 3,4,6-tri-O-acetyl-α-D-pyranosides as secondary products, as previously obtained for H-Beta zeolite-catalysed Helferich glycosylation. It was shown that Fe-Beta zeolite was the more efficient catalyst for this type of reactions, leading to the most efficient methodology for the synthesis of acetylated alkyl 1,2-cis-2-hydroxyglycopyranosides.

2,3-Unsaturated glycosides are valuable synthetic intermediates and constitute the structural units of several antibiotics. Allylic rearrangement of 1,5-anhydro-1,2-dideoxy-1-enitols (glycals) in the presence of a nucleophile, known as the Ferrier rearrangement, generally leads to the formation of 2,3-unsaturated glycosides [32]. Our group reported the synthesis of O- and S-glycosides by reaction of 3,4,5-tri-O-benzyl-D-glucal with different O- and S-nucleophiles (Scheme 3) promoted by zeolites. HY zeolite was the most effective catalyst leading exclusively to the corresponding 2,3-unsaturated O- and S-α-glycosides in moderate yield, expanding the synthetic use of the Ferrier rearrangement to benzyl-protected compounds [25,33].

Hydrolysis of glycosides was also shown to be efficient in the presence of H-form zeolites such as dealuminated HY-FAU with a Si/Al ratio of 15 using water as solvent. Hydrolysis of methyl α- and β-D-glucopyranosides under these conditions led to the corresponding glucopyranoses with a β/α ratio in the range of 5–6, while for the same reaction under homogeneous catalysis the β/α ratio is usually between 2 and 3. This increased rate of hydrolysis for the

β-anomer was ascribed to the increase of stereoelectronic effects, which takes place on a solid surface [34].

3.2. Sugar protection and deprotection

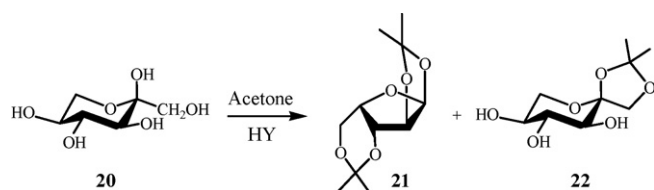#### 3.2.1. Acetonation of monosaccharides

Protection of 1,2- and 1,3-diols via formation of isopropylidene acetals (or acetonides) is one of the most basic reactions in synthetic carbohydrate chemistry [35]. The conventional procedure involves reaction of a sugar diol with acetone or with 2,2-dimethoxypropane, both in the presence of a Lewis or Brønsted acid catalyst under anhydrous conditions. The catalysts employed include sulfuric acid [36], p-toluenesulfonic acid [37], camphorsulfonic acid [38], anhydrous zinc chloride/phosphoric acid [39], anhydrous copper(II) sulfate [40] or anhydrous aluminium chloride [41]. In 1995 our group reported the isopropylidenation of various monosaccharides promoted by the HY zeolite [16]. When D-galactose (14) and L-arabinose (17) were used as starting materials, major formation of the thermodynamically less stable furanose isomers 15 and 18, instead of the expected pyranose diacetonides 16 and 19, was observed (Scheme 4). Acetonation of L-sorbose (20), under similar conditions, led to the first synthesis of 1,2-O-isopropylidene-α-L-sorbopyranose (22) along with the conventionally obtained diacetonide derivative 21 (Scheme 5).
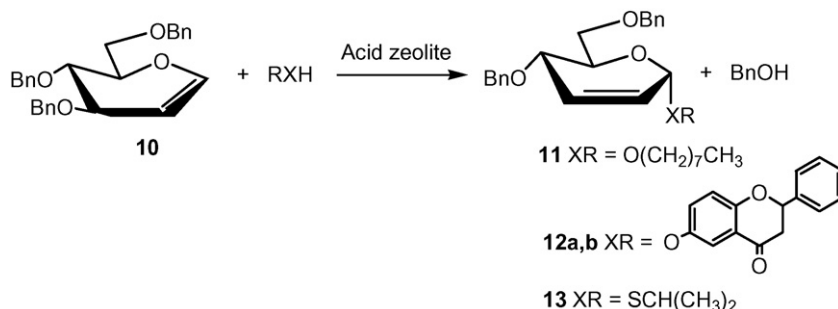
Scheme 3. Ferrier rearrangement mediated by acid zeolites.
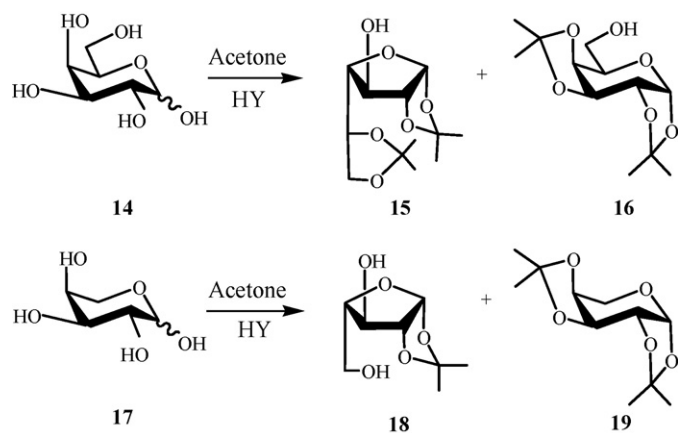
Scheme 4. Acetonation of D-galactose and L-arabinose in the presence of HY zeolite.


Scheme 5. First synthesis of 1,2-O-isopropylidene-α-L-sorbopyranose by acetonation of L-sorbose in the presence of HY zeolite.

### 3.2.2. Acetylation of mono- and disaccharides

Acetylation is a very common method for the protection of hydroxyl groups in organic synthesis [35a] and particularly in carbohydrate chemistry [35c,d]. Acetylated sugars, namely per-O-acetylated monosaccharides, are important intermediates for the synthesis of glycosides, oligosaccharides and glycoconjugates [35c,d,42]. In addition, the introduction of acetyl groups has been a practical method to facilitate the structural elucidation of natural products bearing saccharide moieties. This transformation is often performed using a large excess of acetic anhydride in pyridine, which acts both as a base and as a solvent [43]. Sometimes N,N-dimethylaminopyridine (DMAP) is added as co-catalyst to increase reaction rates [44]. Other catalysts such as sodium acetate [45], iodine [46] and zinc chloride [47] (among a number of other Lewis acids [48]) have been used.

Bhaskar and Loganathan investigated the per-O-acetylation of mono-, disaccharides and methyl glycosides (**23**) with acetic anhydride, over six different acid zeolites [29]. Among the catalysts examined (HY, HEMT, HZSM-5, HZSM-12, HZSM-22 and H-Beta) the large pore zeolite H-Beta presented the best performance, with the highest selectivity providing the formation of the acetylated products (**24**) in good to excellent yield (Scheme 6).

Recently, Gonçalves et al. described the acetylation of glycerol with acetic acid catalysed by different solid acids, including zeolites HZSM-5 and HUSY [49]. Although the conversion using zeolites was lower than the one observed using the other catalysts (Amberlyst-15, K-10 montmorillonite and niobic acid), major for-
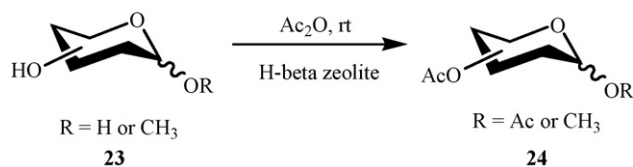
Scheme 6. Per-O-acetylation of monosaccharides and methyl glycosides with acetic anhydride, in the presence of H-Beta zeolite.
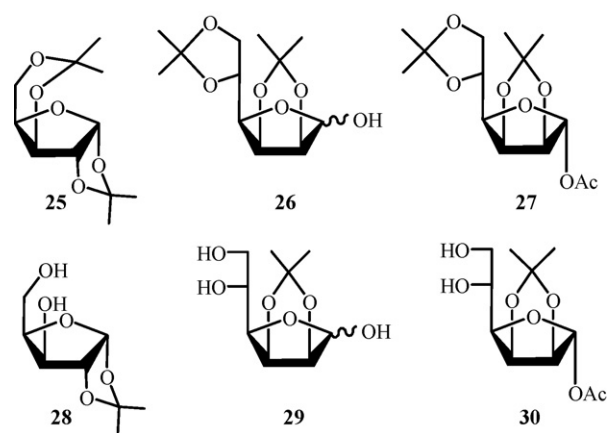
Scheme 7. 5,6-Diols (**28**–**30**) obtained by selective deprotection of the terminal acetonides of **25**–**27**, respectively, using HBEA and HZSM-5 zeolites.

mation (79–83% yield) of the monoacetyl derivative at the primary hydroxyl group was achieved.

3.2.3. Deprotection of di- and tri-O-isopropylidene sugar acetals

The selective hydrolysis of isopropylidene acetals, particularly terminal ones in diacetonide sugar derivatives, has been broadly reported [50]. The catalysts/reagents used include protic acids, namely aqueous hydrochloric acid [50b], 60% aq acetic acid [50c,d], aq trifluoroacetic acid [50e], and Lewis acids, such as BCl$_3$ [50f,g].

Bhaskar et al. achieved the zeolite-catalysed selective hydrolysis of terminal O-isopropylidene sugar acetals derived from D-glucose, D-xylose, D-mannose, and D-mannitol [51]. HBEA and HZSM-5 zeolites proved to be effective in promoting the selective cleavage of the 3,5- or 5,6-O-isopropylidene group of the diacetonide derived furanoses **25**, **26** and **27** to afford the monoprotected derivatives **28**, **29** and **30**, respectively (Scheme 7). However only the HBEA zeolite promoted the hydrolysis of the D-mannitol derived triacetonide to the corresponding di- and monoacetonide derivatives, and no conversion was observed in the case of HZSM-5 catalysed reaction.

3.3. Oxidation

Oxidation has been largely used in carbohydrate chemistry and various procedures have been developed [35c,52]. This transformation can be achieved by chemical methods or by biochemical processes including enzymatic catalysis, such as the oxidation of glucose to gluconic acid [53], an intermediate in food and pharmaceutical industries.

Although homogeneous catalysts are often used in many oxidation procedures, the use of heterogeneous catalysis in oxidation of carbohydrate derivatives has proved a feasible alternative [54]. Hourdin et al. reported the Ruff oxidative degradation of aldonic acids by titanium(IV)- and copper(II)-containing zeolites [55,56]. In the case of the titanium-containing zeolites, the oxidative degradation of calcium D-gluconate to D-arabinose with hydrogen peroxide was performed over EuroTS-1 (a small pore titanium-silicalite), Ti-BEA and Ti-FAU [55]. Only the large pore zeolites were active, even though the product was recovered in low yield (12–17%). The titanium species present in the solution proved to be responsible for the catalytic activity observed. Better arabinose yields were obtained when the reaction was carried out in the presence of copper(II)-containing zeolites. Different zeolite structures were tested, including mordenite, LTL, BEA, MFI and faujasite. The lowest conversion (37%) was obtained using the copper-containing mordenite zeolite, which may be due the monodirectional porosity of this solid, causing limitation to the diffusion rate of the gluconate. The large pore zeolite BEA and the small pore zeolite MFI

proved also to be very effective, although with the latter the reaction efficiency seems to be more dependent on the presence of the copper(II) cations in solution than on the porosity constrains of the zeolite. The best results (63% arabinose yield) were obtained when copper(II)-exchanged faujasite was used as catalyst. The efficiency of the reaction arises from the dissolution of Cu(II) cations from the zeolite.

4. Application of zeolites for carbohydrate-derived raw materials

Carbohydrates are the main source of materials employed for the production of products based on renewable resources, sucrose and starch being the two major supplies. Moreover, polysaccharides such as inulin are gaining importance as a source of fructose. Many catalytic routes have been explored for the transformation of biomass into fine chemicals and have been recently reviewed [57a,b]. In particular van Bekkum and Besemer [58] and Lichtenthaler and Peters [59] revised the application of carbohydrates as raw materials for chemical industry.

Sorbitol can be obtained from starch-derived polysaccharides using ruthenium supported on acid Y-zeolite in the presence of H_2. The acid sites of the zeolite catalyse the polysaccharide hydrolysis yielding transiently glucose, which is immediately hydrogenated to sorbitol on ruthenium [60].

Inverted sugar, which is a 1:1 mixture of glucose and fructose, is usually obtained by hydrolysis of sucrose, and enzymes are the most used catalysts for this transformation on an industrial scale. Moreau et al. reported the hydrolysis of sucrose in the presence of H-form zeolites such as HBEA, HMFI, HMOR and HY-FAU. All catalysts led to the hydrolysis, and at the same time, they acted as specific adsorbents of coloured by-products formed during the reaction. Hence, this proved to be an alternative methodology for the production of colourless inverted sugars, HY-FAU (Si/Al = 15) being the catalyst that offered a better balance between activity, selectivity and by-product formation [61]. H-form zeolites also proved to be efficient for the highly selective production of glucose from insoluble cellulose. This mildly hydrothermal method can become one of the key technologies for a future sustainable society using cellulose biomass [62].

Drastic dehydration of carbohydrates leads to formation of furan compounds such as 2-furaldehyde (**31**) and 5-hydroxymethyl-2-furaldehyde (**32**), (Scheme 8), which are essential intermediates for the production of liquid alkanes and for manufacture of phenolic resins [63a,b]. In addition, 5-hydroxymethyl-2-furaldehyde showed its importance as scaffold for the generation of disubstituted furan derivatives, which are important components of pharmacologically active compounds [63b]. Moreover, derivatives such as 2,5-bis(hydroxymethyl)tetrahydrofuran or 2-hydroxymethyl-5-vinylfuran can be used as starting materials in the preparation of polyesters or epoxy resins, respectively [63b].
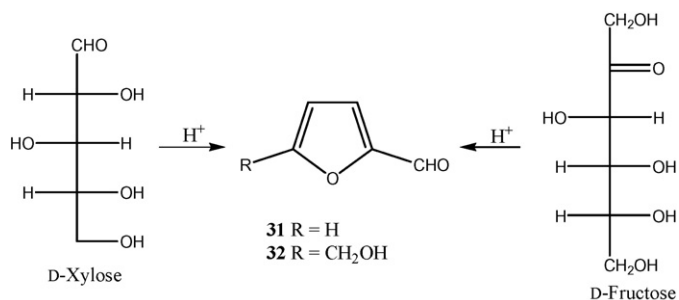
Zeolites exhibit several advantages, when compared to catalysts such as mineral acids or ion-exchange resins used for dehydration of fructose to give 5-hydroxymethyl-2-furaldehyde [15,63]. H-form mordenites with Si/Al ratio of 11 gave a higher conversion rate of fructose. In addition, the highest selectivity (>90%) to 5-hydroxymethyl-2-furaldehyde, observed for H-mordenites with low mesoporous volume, is related to shape selectivity properties within the bidimensional structure of these zeolites. These results, presented by Moreau et al. [64], proved to be promising and competitive with those previously reported and patented for dehydration of fructose to 5-hydroxymethyl-2-furaldehyde on a pilot scale. Moreover the same methodology was applied to the dehydration of D-xylose to furfural and once again H-mordenite with Si/Al ratio of 11 gave the highest selectivity when compared to that achieved with different HY-faujasites [65].

Zeolites A (molecular sieves 3 Å, 4 Å and 5 Å), whose pore dimensions preclude absorption of molecules larger than water or methanol, is typically used only as a water scavenger. Wiśniewski and co-workers [66a,b] reported the thermal cyclodehydration of pentitols (e.g. D-arabinol, D-ribitol and D-xylitol) and hexitols such as galactitol, D-glucitol and D-mannitol performed over these materials in solvent free conditions to achieve monoanhydroalditols and dianhydroalditols with retention or inversion of configuration of the asymmetric carbons.

In order to prepare surfactants from biomass, Corma et al. [67] made use of acid zeolites as catalysts of an innovative two-step cascade route using sorbitol as starting material. Various zeolites were employed namely H-Beta, mordenite and delaminated zeolite ITQ-2 to promote the ketalization of sorbitol followed by direct esterification with oleic acid. All the catalysts provided the selective formation of monoesters in moderate to good yields. The activity of the catalysts was ascribed to be dependent both on their acidity and pore structure.

5. Conclusions

A significant number of research reports dealing with the application of zeolites in synthetic carbohydrate chemistry have been made during the last decade. The use of these materials in the transformation of carbohydrates offers easy and environmentally acceptable procedures, making them suitable catalysts particularly for reactions requiring acidic conditions. In addition to these aspects, their potential to direct stereo- and regioselective controlled reactions opens the opportunity of developing new and efficient approaches for accessing many important carbohydrate derivatives. This review has demonstrated the progress that has been made in this field, notably the employ of zeolites as catalysts in glycosylation reactions, protection/deprotection of hydroxyl groups or hydrolysis/dehydration of carbohydrate raw materials. Nevertheless, development of new applications of acid zeolites in carbohydrate chemistry remains a key challenge for selective, more efficient and safer synthetic methodologies.

Zeolite unique features contribute to an exciting interplay of chemistry, processes and products and these materials are also very promising for large scale processes for the clean synthesis of fine chemicals derived from carbohydrates.

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Scheme 8. Dehydration of D-xylose and D-fructose to 2-furaldehyde (**31**) and 5-hydroxymethyl-2-furaldehyde (**32**), respectively.

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