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Current perspectives on microwave-enhanced reactions of monosaccharides promoted by heterogeneous catalysts

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1. Introduction

In the context of the valorisation of carbohydrates issued from hydrolysis of renewable lignocellulosic feedstocks, chemical derivatisations of mono- and polysaccharides constitute a subject of special relevance. Many of these chemical transformations (*e.g. O*-glycosylations, hydroxyl protections/deprotections, esterifications, dehydrations, and isomerisations) require acid (or base) catalytic systems. In order to develop eco-friendly processes, easily transferable at industrial scale, research has readily shifted toward the exploitation of heterogeneous catalysts as alternative to the traditional homogeneous promoters. In this context, alumina, zeolites and other siliceous-based materials, known for their non-toxic and non-corrosive characters, have attracted a lot of emphasis as catalysts in carbohydrate chemistry, allowing mild reaction conditions and the possibility of easy recovery post-reaction (with eventual reuse) [1].

On the other hand, application of microwave (MW) irradiation as a non-conventional heating source has surged in popularity since the pioneering works of Gedye and Giguere [2]. The claimed cleaner reaction profiles of MW heating, generally accompanied by and probably connected to improved yields and purities, have been widely exploited for achieving general synthetic transforma-

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ABSTRACT

Involvement of heterogeneous catalysts as promoters of carbohydrate conversions, in synergy with microwaves as the heating source, is reported. This paper deals with the application of ion-exchange resins, zeolites, clays and metal oxides as convenient mediators for key transformations of carbohydrates. A special emphasis is placed on the use of (doped) mineral supports, in solventless conditions, as clean promoters in combination with microwave dielectric heating.

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tions [3]. The nature of the microwave enhancement is usually attributed to several specific "thermal effects" that cannot be emulated through conventional heating methods, such as: (i) the elimination of thermal wall effects, (ii) the selective heating of particular reaction components or (iii) the rapid heating rates and the possibility of temperature gradients.

In the myriad areas of chemical synthesis, microwave technology has however suffered a certain delay in the field of carbohydrate chemistry. Nevertheless, its application is nowadays more documented for making a range of new added-value sugars entities [4].

We present therefore an overview, along with original results, of key microwave-assisted transformations of mono- and polysaccharides mediated by heterogeneous catalysts [5]. Rather than attempting to provide an exhaustive treatment, we have selected three benchmark reactions for this review, namely protection/deprotection of hydroxyl groups, (Fischer) *O*-glycosylation and dehydration reaction. Comparison with classical homogeneous catalysts and conventional heating methods (*i.e.* oil bath), in terms of yields and selectivities, is proposed for these relevant examples. Recent developments regarding the original use of carbon-based catalysts in carbohydrate chemistry are also reported.

2. Synergy between microwave heating and heterogeneous catalysts

In contrast to conventional homogeneous synthetic pathways, the use of eco-compatible surface active heterogeneous cata-



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Scheme 1.

lysts have gained appreciable attention in recent years [6]. The tandem use of microwaves and polymer-grafted catalysts or promoters immobilised onto inorganic supports has thus blossomed into a powerful protocol because of the enhanced selectivity and milder conditions usually applied [7,8]. Practically, inorganic backbones like silica, alumina, aluminosilicates, clays or some polar polymers are well-suited under microwave conditions [9]. When properly dried, these materials display, however, poor MW absorption ability and are weak thermal conductors, with loss tangent of 2×10^{-4} @100 MHz for Al₂O₃, 2×10^{-5} @1 MHz for fused silica and 1×10^{-4} @100 MHz for polystyrene (compared to 4×10^{-2} @1 MHz for water) [10]. When doped or impregnated (with homogeneous Brönsted/Lewis catalysts or metal/metal oxides mediators), these supports display conversely improved microwave absorption properties, generating local superheated regions (referred as "hot spots") [11]. These hot spots may induce a reorganisation of the catalyst under microwave conditions and are probably responsible for reaction rates and selectivity enhancement (compared to conventional heating at the same nominal temperature) [12,13].

The involvement of such heterogeneous catalytic systems under microwave conditions represents an innovative approach with processing advantages. These solid-state catalysts find scope in the context of green chemistry development as they are active in solvent-free or dry media synthesis, with potential advantages in terms of separation, recovery post-reaction and recycling assays [9]. The creation of hot spots, specific under MW conditions, is typically utilized for energy saving as improved yields and selectivities are recorded after shorten reaction times at lower nominal temperatures. This strategy is particularly adapted in carbohydrate chemistry where conventional heating protocols upon extended exposure to higher temperatures usually encounter degradation of saccharides.

3. Microwave-mediated hydroxyls protection/deprotection

Most common monosaccharides contain several hydroxyl groups which are difficult to chemically differentiate. Hence, the classical methods needed to modify these hydroxyls in a regio-controlled manner are tedious and complex [14]. Microwaves have therefore readily emerge as an efficient and useful methodology to assist protecting group selective manipulations on saccharides, as shorter reaction times, better yields and improved stereo- and regio-selectivities are mostly encountered using lower catalyst loadings [15].

3.1. Acylations using polymer-supported catalysts

Oscarson et al. have reported on the convenient application of microwave dielectric heating for the treatment of 1,2:5,6di-O-isopropylidene- α -D-glucofuranose **1** with acetyl chloride or pivaloyl chloride and catalytic amounts of base promoter (Scheme 1). Results are quite interesting, demonstrating the benefits of microwaves in terms of acceleration of reaction rates and improved yields, as the corresponding 3-O-protected target is isolated in good yields after 20 min of MW exposure (Table 1). Of

Table 1

Microwave-assisted acylations of **1** with acetyl chloride or pivaloyl chloride in basic conditions^a.

Reagent	Base catalyst	<i>T</i> (°C)	Time (min)	Product	Yield (%)
AcCl	Pyridine	170	12	2	80
AcCl	PS-DIEA	165	20	2	66
AcCl	PS-DMAP	180	15	2	88
PivCl	Pyridine	160	10	3	68 ^b
PivCl	PS-DIEA	160	20	4	79
PivCl	PS-DMAP	180	15	4	88 ^c

^a Experimental data are extracted from Ref. [15].

^b Yield inclusive of **3**+**4**=85% (**3**:**4**=3:1). Reaction under "classical" conditions: after 2160 min at r.t., yield in compound **3** reached 82%.

^c Yield in compound **4**: 88% after 300 min at r.t.

special interest is the grafting of sterically hindered pivaloate functions, which is almost completely restrained under classical conditions [15]. This pivaloate esters formation is a clear evidence of how microwaves can extend and enhance processes that are prohibitively long or low yielding using conventional heating methods.

use of supported polystyrene-bases, The i.e. N.N-(diisopropyl)aminoethylpolystyrene (PS-DIEA) and N-(methylpolystyrene)-4-(methylamino)pyridine (PS-DMAP), as alternatives to pyridine, evidences somewhat slower reactions but still fast compared to conventional heating methods. Whilst a 5,6- to 3,6-acetal migration prior to acylation is observed for MWassisted pivaloylation of **1** in the presence of pyridine, probably catalysed by the *in situ* formed pyridinium chloride, this acetal migration is advantageously inhibited using such solid supported base instead of free pyridine.

3.2. Deacylation vs. deacetalation using K10 clay

There are numerous methods reported in the literature for the deprotection of carbohydrates under both acidic and basic conditions [16]. Typically, Na₂CO₃, Et₃N, KCN, hydrazine and I₂ are employed in aqueous media for such (regioselective) deprotection studies. Interesting, however is the use of Montmorillonite K10 clay, alumina and polymer-supported reagents as mild deprotecting agents under microwave heating. Indeed, the method described by Mori and Tsuzuki [17], involving 1 equiv. of Et₃N in a 5:1 MeOH/H₂O mixture, affords compound 7 in 78% yield when saccharide 5 is exposed at 150 °C in the microwave cavity for a runtime of 15 min. By contrast, when using K10 clay as the promoter, under exactly the same conditions, deacetalation occurs preferentially to debenzoylation and derivative 8 is isolated in 89% yield after only 2 min (Scheme 2). Moreover, as polymer-supported reagents provide good results for acylations, Oscarson describes the quantitative hydrolysis of acetal 6 in ethanol/water with polymer-anchored PPTS [poly(4-vinylpyridinium-p-toluenesulfonate)] at 150 °C for 2 min (Table 2) [15]. No alteration of the initial anomeric configuration is observed under MW conditions.

Noteworthy is also the approach devised by Ley and Mynett dealing with the use of recyclable neutral alumina to hydrolyse a series of pivaloyl protected alcohols (referred as Varma's conditions). [18,19] This strategy is clean, cost-effective and high-



Scheme 2.

Table 2

Microwave-mediated deacetalation or deacylation in the presence of solid promoters. $^{\rm a}$

Saccharide	Catalyst	Time (min)	Product	Yield (%)
5	Et ₃ N	15	7	78
5	K10 clay	2	8	89
6	Poly-PPTS	2	9	94

^a Experimental data are extracted from Ref. [15]. Reaction temperature was fixed at 150 °C.



Scheme 3.

yielding, preventing both group migration and anomeric centre isomerisation. Such a treatment using an alternative heating source (*i.e.* oil bath up to $75 \,^{\circ}$ C) could not be achieved.

4. *O*-glycosylations under microwave conditions promoted by various solid acids

4.1. Lewis acid impregnated on mineral supports

O-Glycosylation, i.e. specific derivatisation of the anomeric hydroxyl position, is one of the most thematic study in the field of carbohydrate chemistry [20,21]. Basically, in a typical Fischer O-glycosylation, alkyl chains are appended specifically at the C-1 position via an acid-catalysed treatment of totally O-unprotected monosaccharide with a slight excess of alcohol in anhydrous conditions, whilst Helferich-type glycosylation involves completely O-protected donors (Scheme 3) [22,23]. The pioneering work in MW-assisted O-glycosylations has been accomplished by Cléophax et al. in 1997 using homogeneous Brönsted or Lewis acids as well as solid promoters (zeolites, montmorillonites or ion-exchange resins) [24]. Starting from D-glucose 10, yields in adduct 12 (a potent surface-active agent) culminate up to 15% (mainly due to glycoside decomposition in acidic pH during the run) after 10 min at 150 °C. Result is noteworthy when compared to other "classical" multi-step protocols or enzyme-catalysed glycosylations, but this approach is not totally satisfactory [25].

The reaction of *n*-decanol with the peracetylated form **11** promoted by ZnCl₂, free or adsorbed on several inorganic supports, demonstrates better outcomes notably due to the increase thermalstability of adduct **13** (Table 3) [24]. Homogeneous zinc chloride is the most convenient catalyst for this reaction affording **13** in 74% yield, mainly as the α -pyranose anomer, after only 3 min of MW exposure. The impregnation of this Lewis acid onto mineral support

Table 3

Microwave-induced Fischer O-glycosylation of n-decanol with **11** mediated by $ZnCl_2$ adsorbed on several mineral supports^a.

Catalyst	$T(^{\circ}C)$	Time (min)	Yield (%)	lpha: eta ratio
ZnCl ₂ (1 equiv.) ^a	113	300	25	21:4
ZnCl ₂ (1 equiv.) ^b	113	3	74	64:9
ZnCl ₂ /silica gel (1 g/5g)	100	11	30	16:14
Clayzic ^c	115	11	20	16:4
ZnCl ₂ /sand (1g/5g)	125	8.5	58	30:28

^a Alkylation of **11** in the presence of 1.5 equiv. of *n*-decanol. Reactions performed in closed vessels conditions. Data are from Ref. [24].

^b Comparative reaction performed in an oil-bath.

^c ZnCl₂ adsorbed onto Montmorillonite K10.

Table 4

Microwave-assisted O-glycosylation of *n*-decanol with D-glucose **10** mediated by H_2SO_4 adsorbed on several inorganic supports^a.

Catalyst	Yield (%)	α : β ratio
35 wt% H ₂ SO ₄ /SiG ₆₀ ^b	82	55:45
50 wt% H ₂ SO ₄ /SiG ₆₀	63	55:45
70 wt% H ₂ SO ₄ /SiG ₆₀	41	55:45
35 wt% H ₂ SO ₄ /MCM-41	94	55:45

^a Reactions are performed using a Milestone STARTS microwave reactor, in closed vessels conditions, at 100 °C for 10 min. Temperature is monitored using an optic-fiber. After reaction, the catalyst is eliminated by filtration and the crude reaction mixture chromatographied on silica gel. α : β ratios are estimated by ¹H NMR at 25 °C. Anhydrous D-glucose, *n*-decanol (5 equiv.), catalyst (0.25 equiv.).

^b H₂SO₄ loading = 35 g/100 g of final catalyst. For preparation, characterisation and composition of each catalyst, see Ref. [27].

(*i.e.* silica gel, sand or K10 clay) results however in lower yields but offers obvious work-up and purification advantages.

4.2. Acidic ion-exchange resins

Of interest also is the microwave-accelerated Fischer-type O-glycosylation protocol proposed by Bornaghi et al. and involving Amberlite acidic ion-exchange resin as the promoter [21c]. The anomeric derivatisation of various substrates (D-glucose, D-mannose, D-galactose, N-acetyl-D-glucosamine and N-acetyl-Dgalactosamine) with representative short-chain alcohols (MeOH, EtOH, allyl alcohol or benzyl alcohol) is both practical and efficient (with less than 5% of starting saccharide remaining after 10 min at 90 °C). An impressive increase of reaction rates is thus encountered (minutes compared to hours under classical heating) with preferential formation of the α -adduct. At the opposite, the β -anomer is selectively isolated for derivatisation of monosaccharides with long-chain alcohols (with a C_8 - C_{12} alkyl chain) but yields remain extremely moderate (<10-20%) [26]. The high viscosity of the reaction medium (even up to 90 °C) combined to the fact that Amberlite IR120 resin is considered to be useful below 120 °C are indeed two major drawbacks which can greatly limit the process implementation.

4.3. Brönsted acids immobilised on silica

Recently, we disclosed on the use of mineral silica-based supports doped with Brönsted acids as efficient promoters for one-step *O*-glycosylation of totally *O*-unprotected uronic acids donors (in order to produce, in solventless conditions, suitable biosurfactants) [27]. These heterogenised Brönsted acids (including H_2SO_4 , H_3PO_4 or Keggin-type heteropolyacids) on silica are usually superior proton sources compared with other acidic solids or resins (including Nafion-H or polystyrene sulfonic acid) when examined under heterogeneous conditions [28]. Advantageously, these catalysts impregnated on silica supports are thermostable and offer good mechanical stability with potential advantages in manufacturing scale synthesis [29].

It is interesting to notice that these catalysts exhibit also an activity for the microwave-promoted derivatisation of D-glucose **10** with *n*-decanol (Table 4). Our experiments highlight that few minutes of microwave exposure are enough to convert **10** into its corresponding long-chain glycoside **12** as its pyranosidic form. Using H₂SO₄ with 35 wt% loading on silica gel as the promoter, compound **12** is isolated in 82% yield. When increasing the quantity of sulfuric acid onto the mineral support, yield is substantially reduced (mainly due to the decomposition of starting D-glucose by browning reaction in the early stages of the process). Surprisingly, α and β anomers are isolated in a quite equimolar ratio, whatever the catalytic system employed. This observation in terms of anomeric ratio joints aforementioned experiments with ZnCl₂ impregnated

on silica gel and illustrated in Table 3. Of special interest is the use of molecular sieve of the MCM-41 type as support, as yield in *n*-decyl-glycoside reaches unprecedented value of 94% after only 10 min of MW exposure.

Although microwaves have been widely exploited for these *O*-glycosylations, it should be pointed out that its application is still practically limited to a few case studies. Furthermore, the nature of the alcohol selected (in terms of polarity, melting point or viscosity properties) has a direct impact over selectivities, yields and decomposition rates, but this observation is not entirely rationalised [30]. Moreover, attempts to scale-up Fischer *O*-glycosylations (promoted by homogeneous acids) were proposed 10 years ago by Loupy [31] and Nüchter [32] 0.1 and 1 kg-scale of **10** (or peracety-lated adduct **11**), respectively. Even if results were at first sight promising, this microwave-mediated Fischer-type glycosylation seems nowadays to fall into disuse.

4.4. Sulfuric acid impregnated on carbon

Even though promising, silica-supported catalysts (H_2SO_4/SiG_{60}) are poorly suited for consecutive batch *O*-glycosylations, as a low leaching of H_2SO_4 is encountered during the run [27]. An ideal solid substitute acid for such a microwave application should therefore combine high efficiency and thermostability while maintaining strong acidity even in water-containing media. Moreover, for impregnated catalyst, the support should fulfill several requirements as chemical inertness, steady mechanical and physical properties and low environmental impact.

Recently, Yuan et al. have reported on the application of sulfuric acid loaded onto wooden activated carbon (H_2SO_4/C) for the microwave-promoted production of fatty acid methyl esters [33]. The choice of this catalytic system is judicious as carbon is commonly employed as a suitable support for many academic and industrial relevant catalysed applications [34]. On the other hand, activated carbon is defined as an excellent absorber of microwave energy, with a dissipation factor substantially higher than most solvents [35]. Favorably, unique overheating of the surface of the carbon-based material, which cannot be duplicated by conventional means, is encountered [36]. Since H_2SO_4/C has hitherto never been used in the field of carbohydrate chemistry, we check herein its potential as an efficient catalyst for the microwave-assisted synthesis of added value derivatives of D-glucuronic acid.

Even if not satisfactory for long-chain glycosides production (yield in adduct **12** of 27% after 10 min of MW reaction at 100 °C, α : β = 30:70), activated charcoal loaded with sulfuric



acid (H₂SO₄/C) appears as a convenient heterogeneous promoter for the microwave-assisted one-step production of monosubstituted β-D-glucofuranosidurono-6,3-lactones from *O*-unprotected D-glucuronic acid **14** (Scheme 4). These lactones are not easily attainable under classical heating conditions, as difunctionalised α ,β-pyranosidic and α ,β-furanosidic isomers are usually recovered as side-products [27]. Conversely, using microwaves in combination with H₂SO₄/C as the promoter, yields in lactonic compounds **15–21** culminate around 85–99% after 10 min of reaction at 60 °C and anomeric selectivities are in favor of the β-anomer (Table 5). No trace of disubstituted isomers is encountered under MW, whatever the reaction conditions employed (catalyst loading, temperature or runtime).

In order to highlight the beneficial effect played, on the one hand, by microwaves and, on the other hand, by immobilisation of the acid catalyst, we carried out two sets of additional experiments. In the first series, microwave-assisted reaction between D-GlcA and 3-chloro-1-propanol mediated by H_2SO_4/C is compared to the same reaction conducted in a thermostated oil bath under otherwise identical conditions (concentration, temperature, etc.). In the second series, ability of H_2SO_4/C and H_2SO_4 to promote MW-assisted formation of 3'-chloropropyl D-glucofuranosidurono-6,3-lactone **19** is evaluated. Results are summarised in Fig. 1.

Firstly, our results clearly evidence that microwave irradiation is somewhat superior to conventional heating. Indeed, under microwave conditions, D-GlcA conversions are the follows: 50%, 70% and 99% for runtimes of 1, 5 and 10 min, respectively, *vs.* 19%, 56% and 71% for conventionally heated reactions. Noteworthy is also the observation that microwaves lead to adduct **19** predominantly as the β -anomer, whilst conventional heating provides **19** as a 40:60 α : β mixture, contaminated by traces of disubstituted by-products. We also observe that the origin is not intercepted in the plot of ln([GlcA]₀/[GlcA]_t) *versus* time plot for the reactions per-

Table 5

Microwave-assisted conversion of D-glucuronic acid 14 in ROH media catalysed by sulfuric acid loaded onto silica-based supports or activated charcoal^a.

(%) ^b

^a Reactions are performed using a CEM Discover microwave reactor, in closed vessels conditions. Temperature is monitored using an infrared detector. After reaction, the catalyst is eliminated by filtration and the alcohol is removed under vacuum or by chromatographic separation. D-Glucuronic acid, alcohol (5 equiv.), acid catalyst (0.2 equiv.). Catalyst composition: 35 wt% H₂SO₄ loaded onto the mineral support.

 $^{b}\,$ Isolated yield of pure β anomer after chromatographic purification on silica gel.

^c In an oil-bath, after 10 min at 85 °C, using the same reagents quantity, product **16** was solely formed in 68% yield (α : β =20:80).

^d After 10 min at 60 °C in an oil-bath, yield in **17** reached 42% (α : β = 10:90).

^e After 10 min at 60 °C in an oil-bath, yield in **19** reached 70% (α : β =40:60).



Fig. 1. Time dependence of conversion (left) and $\ln([GlcA]_0/[GlcA]_t)$ where $[GlcA]_t$ are the D-glucuronic acid concentration at times 0 and t (right) for the addition of 3-chloro-1-propanol to D-GlcA catalysed by H_2SO_4/C (\odot ; y = 0.586 + 0.125 x, $r^2 = 0.998$) or H_2SO_4 (\odot ; y = 0.033 + 0.153 x, $r^2 = 0.999$) under microwave irradiation or under conventional heating in an oil bath in the presence of H_2SO_4/C (\odot ; y = 0.326 + 0.146 x, $r^2 = 0.989$). Reaction conditions are the same as in Table 5.

formed under microwaves. For instance, reaction performed during only 1 s (as programmed in the microwave set-up) reveals already D-GlcA consumption of 42%. For sake of understanding, it should first be mentioned that the CEM Discover oven used in this study is programmed so as t = 0 when the required 60 °C is reached and not when irradiation starts. Practically, the microwave reactor takes 2–5 s to reach the requested temperature. When tests are performed under conventional heating, reaction begins directly with the immersion of the tube in the oil bath. The D-GlcA conversion is obviously zero at t = 0.

Secondly, comparison between homogeneous sulfuric acid and its supported version is undeniable, mainly in the early stages of the process. As adduct **19** is recovered in 51% yield after 1 min using H_2SO_4/C , yield drops to 36% when using liquid H_2SO_4 solution as the promoter. Moreover, formation of unwanted by-product **16** is encountered when using homogeneous H_2SO_4 .

5. Dehydration reactions

The catalytic dehydration of fructose precursors into 5hydroxymethylfurfural (5-HMF) has received considerable attention within the last decade (Scheme 5). 5-HMF is a potent biomass-derived chemical, suitable intermediate for fine chemicals, pharmaceuticals or furan-based polymers [37]. Its production has been widely studied, using conventional heating, as in homogeneous (H₂SO₄, H₃PO₄, HCl, oxalic acid, and levulinic acid) than in heterogeneous acidic conditions (H-form zeolites, acid cation exchange resins, and transition-metal salts) [38,39]. Homogeneous acid catalysed processes are usually effective (*e.g.* 40–60% 5-HMF yields associated to high fructose conversions) but have major drawbacks in terms of acid recovery and equipment corrosion. On the other hand, the use of solid acids offers work-up advantages and



Scheme 5. D-glucose production is a consequence of fructose isomerisation; levulinic acid and formic acid are obtained by rehydration of 5-HMF.

high 5-HMF selectivities but only low fructose conversions (about 30–60%) are measured, even after extended reaction times (up to 2 h).

Recent reports have underlined that significant energy savings could be achieved using microwaves as the heating source for performing this heterogeneous catalytic dehydration of fructose, either in water, organic solvents or in organic-water systems [40,41]. Even if fructose conversion is much more higher for homogeneous acid-catalysed processes, microwaves have a beneficial impact over 5-HMF yields for reactions with heterogeneous promoters (Table 6). Noteworthy is the investigation carried out by Qi and co-workers and demonstrating the usefulness of a strong acid cation-exchange resin at a temperature of 150 °C. In this context, fructose conversion reaches more than 95% after a runtime of 15 min and is associated with 5-HMF yields culminating at about 70–75%. For sake of comparison, after a reaction time of 10 min, vield in 5-HMF attains 13.9% under conventional heating conditions, whilst 5-HMF is isolated in 70.3% yield after microwave exposure under identical conditions (reagents concentration, reaction time and temperature) [40]. The use of transition-metal oxides (ZrO₂, anatase or rutile TiO₂), impregnated or not with sulfuric acid, is considered as active in terms of fructose conversions, with a

Table 6

Microwave-assisted conversion of fructose into 5-HM	F catalysed by several heterogeneous	s promoters in water, organic solvents or mixtures.
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Catalyst	Solvent	Fructose (wt.%)	<i>T</i> (°C)	Time (min)	Fructose conversion (%)	5-HMF yield (%)	Ref.
H ₃ PO ₄	H ₂ O	0.9	240	2	98.0	65.3	[42]
Zeolite	H ₂ O-MIBK	1.7	165	60	76.0	69.2	[38a]
IER ^a	H ₂ O-DMSO/PVP ^a	10	90	480	76.0	58.5	[38b]
IER ^b	H ₂ O-acetone ^b	2	150	15	95.1	73.4	[40]
SO ₄ ²⁻ /ZrO ₂ ^c	H ₂ O	2	200	5	79.9	29.9	[41]
SO ₄ ²⁻ /ZrO ₂ ^c	Acetone–DMSO ^d	2	180	5	91.3	65.6	[41]
ZrO ₂	H ₂ O	2	200	5	83.6	38.1	[43]
TiO ₂	H ₂ O	2	200	5	65.3	30.6	[43]

^a Ion-exchange resin PK-216 used in an aqueous phase with DMSO and poly(1-vinyl-2-pyrrolidinone) (PVP).

^b Ion-exchange resin Dowex 50wx8-100 used in a water-acetone 30:70 (w/w) mixture.

^c Catalyst prepared by impregnation of zirconium hydroxide with H₂SO₄. Prior to use, the catalyst is calcinated at 600 °C. Calcination temperature is demonstrated to have an impact on the outcome of the reaction.

^d Acetone/DMSO 70:30 (w/w).



maximum 5-HMF yield of 65% in a water-acetone mixture. Advantageously also, both ZrO_2 and TiO_2 (or based catalyst) are found to effectively suppress the subsequent rehydration of 5-HMF into levulinic acid and formic acid during the run [41]. Work with Dglucose as the starting material is found to be less profitable, as D-glucose conversions of about 57–64% associated to 5-HMF yields of 10–18.6% are obtained, respectively with ZrO_2 and TiO_2 , after 5 min of MW exposure at 200 °C.

6. Current trends and future perspectives

In the present economical and environmental context, there are strong incentives to convert bio-based resources into valuable products via suitable, ideally "one-pot" and solvent-free, processing routes [44]. Thereby, the development of both innovative catalytic strategies and alternative reaction conditions (including notably MW or sonication, and either ionic liquids or supercritical fluids as solvents) have attracted extensive R&D efforts [45].

As far as carbohydrates are concerned, we mention herein two original synthetic approaches for the conversion of renewables into platform molecules using solid catalysts in synergy with microwaves.

Marek et al. investigate recently the one-step microwaveassisted conversion of common monosaccharides (*i.e.* D-glucose, D-fructose, D-mannose and D-sucrose) into lactic (2hydroxypropionic) acid (Scheme 6). Lactic acid, usually obtained via fermentation of glucose or polysaccharides, is employed by NatureWorks (US), Toyota (Japan) or Galactic (Belgium), to produce polylactide (PLA), a biodegradable and recyclable polymer.

As stress is laid on the green character of new processes, this alkaline degradation of monosaccharides is evaluated in solventless conditions. The catalyst employed consists in alumina-supported potassium hydroxide, known to be robust, versatile, easily regenerable and efficient under microwave conditions. A high temperature of 180 °C is shown to induce selective decomposition of the starting sugar into lactic acid in up to 75% yield. Influence of the KOH loading onto the mineral support has been judged to impact over yields [46].

Beside degradation of structurally well-defined monosaccharides, extensive studies are directed toward the straightforward conversion of renewable crude feedstocks into valuable chemicals [47]. Efficient depolymerisation of complex architectures as cellulose, hemicellulose, lignin and starch is thus currently one of the major objective.

For the acid-catalysed saccharification of cellulose, heterogeneous catalysts tend nowadays to substitute traditional mineral ones (H_3PO_4 or H_2SO_4) [48,49]. Microwave dielectric heating plays here a key role in activating cellulose polymers and strengthening effective particle collisions, leading to noticeable acceleration rates effects on this heterogeneous catalytic process. By this way, Wu et al. disclose in 2010 on the environmentally benign MWmediated hydrolysis of cellulose into reducing sugars promoted by a solid biomass char sulfonic acid catalyst (BC-SO₃H) (Scheme 7) [50]. In the same way, Zhang et al. propose the MW-assisted hydrolysis of cellulose, solubilised in ionic liquids, promoted by several H-form zeolites [51]. These approaches are more selective than homogeneous acids related processes as D-glucose is the major sac-



charide isolated, whilst a mixture of components (viz. other sugars, oligosaccharides) are otherwise detected [49].

7. Conclusions

Application of heterogeneous catalytic systems, in synergy with microwaves, is an interesting approach in the field of carbohydrate chemistry to promote key transformations. First, as *O*-glycosylations proceed at moderate temperatures (typically 60–85 °C) for several hours under classical conditions, application of microwave dielectric heating is a convenient solution to considerably reduce reaction times to a few minutes. Secondly, for hydroxyls protection/deprotection, use of "dry media" or solventfree conditions under microwave is an excellent option in the context of developing a green and sustainable chemistry. Finally, for more energy-demanding reactions such as selective conversion of monosaccharides into 5-HMF, microwave treatment offers interesting work-up facilities combined to improved yields and selectivities.

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