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Recent progress in base-catalyzed isomerization of D-glucose into D-fructose

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Development of a catalytic process for isomerization of D-glucose into D-fructose presents a crucial step for valorization of lignocellulosic feedstocks. This review focuses on basic catalysts as highly catalytically active and readily commercially available molecules and materials. The recent publications report that the solid bases catalyze the isomerization mainly heterogeneously with only a minor contribution of catalysis by OH^-. For catalysis by amines, the hydroxide ions are on the contrary believed to be catalytically active species, though selectivity for D-fructose seems to depend on the amine structure. Buffers present another type of soluble basic catalysts which can be readily coupled with a facile separation of D-fructose from the reaction mixture via anionic extraction or adsorption upon complexation with phenylboronic acids.

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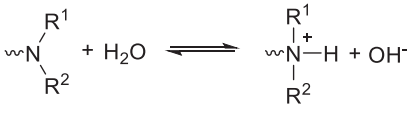
Isomerization of D-glucose (Glc) into D-fructose (Fru) presents a key transformation of Glc, readily obtained upon hydrolysis of cellulose, into valuable platform chemicals, for example, 5-hydroxymethylfurfural (HMF). The isomerization requires a catalyst and can be promoted by an enzyme, a base, or a Lewis acid [1–4]. This opinion piece specifically focuses on the latest results on the isomerization in the presence of base catalysts as highly catalytically active and inexpensive materials. Comprehensive reviews on the isomerization can be found elsewhere [1–4].

The chemically catalyzed isomerization of saccharides was uncovered by Lobry de Bruyn and Alberda van Ekenstein at the end of the 19th century [1]. During the 20th century the mechanism of the isomerization in the presence of bases was intensively studied. The up-to-date version of the reaction mechanism was formulated by de Wit et al. in 1979 [5]. The proposed mechanism (Figure 1S in electronic supplementary information) includes (1) deprotonation of Glc in a pyranose form into cyclic Glc anion; (2) fast equilibrium between the cyclic Glc anion and a pseudo-cyclic carbonyl anion accompanied with a transfer of the negative charge onto O5; and (3) a rate-limiting formation of an enediol anion intermediate via an intramolecular proton shift from C2 to O5. Reversal of these steps led after conformational changes to Fru. NaOH or KOH were used as catalysts in the last century in the majority of works on the isomerization, and literally no focus was placed on a catalyst development.

In 2000, Moreau et al. published for the first time on the catalytic activity of hydrotalcites, alkali- and alkali-earth metal exchanged zeolites as solid catalysts for the isomerization [6]. This publication appeared to be the first one in the series of papers aiming at a design of a solid catalyst for the isomerization. In recent years, materials making use of alkalinity of Mg and Ca have been intensively explored, including MgO [7–9], Mg–Al hydrotalcites [7,9–17], Mg- or Ca-impregnated or exchanged zeolites [18–22], attapulgite [23], MgO–Nb phosphate [24], Mg-containing titanosilicates [25], CaO–ZrO_2 [26], MgO–ZrO_2 [27], MgO/biochar [28], CaO–Al_2O_3 [29], CaO–MgO [30], CaO/C [31], and alkaline earth metal titanates [32]. Soluble amines [33–43] recently attracted attention of researchers, and corresponding N-containing solid catalysts were fabricated [35,36,39,40,44–47]. Catalytic activity of solid bases, such as silicates [48], SiO_2 treated with ammonia [49], zirconium carbonate [50], ZrO_2 [51], and basic hybrid catalysts [52], was reported. Most frequently, the reaction is conducted in aqueous medium, in the temperature range of 80–120°C. Under these conditions, Fru yield is typically limited to *ca.* 30–35%, and selectivity for Fru declines upon increase of Glc conversion. Table 1 summarizes the recently published data on Glc isomerization into Fru in the presence of base catalysts.

Upon immersion in water, the bases react with H_2O generating hydroxide ions OH^- according to various reactions, such as protonation (Eq. (1)) [34], dissociation (Eq. (2)) [53], or hydrolysis (Eq. (3)) [48].



(1)

Table 1

Literature data on catalytic activity of basic catalysts for glucose isomerization into fructose.

Entry	Conditions				Reaction outcome with the best catalyst		Contribution of heterogeneous/homogeneous catalysis				Ref.
	Solvent	T, °C	All the tested catalysts	The best catalyst[a]	Max. Glc conversion, %	Max. Fru yield, % (at Glc conversion)	Leaching (elements)	pH	Test[b]	Heterogeneous or homogeneous catalysis[c]	
Solid bases: hydrotalcites (HT)											
1	H_2O	95	calcined Mg–Al HTs	calcined HT with Mg/Al = 3	42	25 (at 42% conv.)	no	n.d.	n.d.	heterogeneous[d]	[6]
2	H_2O	90	Mg–Al HTs in carbonate, hydroxide, and carbonate-hydroxide form; calcined HT; NaX and KX zeolites	calcined HT[e]	35	25 (at 35% conv.)	no	n.d.	no	n.d.	[12]
3	H_2O	90	Mg–Al HT in carbonate form, calcined and rehydrated HTs	HT in carbonate form	62	42 (at 58% conv.)	Mg	7.3–9	FT	heterogeneous	[10]
4	H_2O	110	Mg–Al HTs in carbonate form	HT[f]	34	30 (at 34% conv.)	Mg	8	FT	heterogeneous	[11]
5	H_2O	120	calcined Mg–Al HT, MgO, MgO/carbon nanotubes, CoMnAlMg mixed oxides	calcined hydrotalcite $(MgO)_{0.7}(Al_2O_3)_{0.3}$	n.d.	27 (at 36% conv.)	Mg	n.d.	no	heterogeneous	[7]
6	H_2O	120	Mg–Al HTs in carbonate form	HT synthesized by AMOST[g]	40	25 (at 40% conv.)	n.d.	n.d.	no	n.d.	[17]
7	DMF	120	Mg–Al HT in carbonate form, calcined Mg–Al HT, calcined and rehydrated Mg–Al HT	Mg–Al HT calcined and rehydrated with sonication-assisted method	n.d.	40 (at 50% conv.)	n.d.	–	no	n.d.	[13]
8	DMF	80	Mg–Al HT in carbonate form, calcined Mg–Al HT, calcined and rehydrated Mg–Al HT	calcined and rehydrated Mg–Al HT	n.d.	35 (at 50% conv.)	n.d.	–	no	n.d.	[14]
9	EtOH	120	Mg–Al HT with different anions in interlayer	Mg–Al HT in carbonate form	80	56 (at 70% conv.)	n.d.	–	no	heterogeneous	[15]
10	1-butanol	120	Mg–Al HT calcined and rehydrated with sonication-assisted method	Mg–Al HT calcined and rehydrated with sonication-assisted method	85	56 (at 80% conv.)	no	–	No	heterogeneous	[16]
Solid bases: zeolites											
11	H_2O	95	Li-, Na-, K-, Cs-, Ca-, and Ba-exchanged A, X, and Y zeolites	NaX, KX[h]	n.d.	17-18 (at 20–23% conv.)	alkali- and alkali-earth metals	n.d.	No	heterogeneous[d]	[6]
12	H_2O	100	zeolites with hierarchical MFI structure and alkali (M = Na, K) and alkaline earth metals (Me = Ca, Mg)	MgK-zeotype catalyst[i]	ca. 50	30 (at 45% conv.)	Na, K, Mg, Ca	n.d.	FT	heterogeneous with a contribution of homogeneous catalysis	[21]
13	H_2O	100	Mg-impregnated NaY	Mg-impregnated NaY	49	32 (at 45–49% conv.)	Na, Mg	n.d.	CT	heterogeneous with a contribution of homogeneous catalysis	[19]
14	H_2O	100	Mg-impregnated NaY, NaMOR, NaBEA, NaZSM-5, and NaFER	5%MgNaY	38	34 (at 38% conv.)	Na, Mg	n.d.	CT	heterogeneous with 9–18% contribution of homogeneous	[18]
15	H_2O	100	Mg-impregnated desilicated NaY	5%MgNaY0.02[j]	51	35 (at 41% conv.)	Na, Mg	n.d.	CT	heterogeneous with 6–16% contribution of homogeneous	[20]
16	H_2O	75–100	Mg- or Ca-impregnated desilicated (Na, K)BEA	MgK-DBEA	50	31 (at 31% conv.)	Na, K, Mg, Ca	n.d.	CT	no contribution of homogeneous catalysis for MgK-DBEA	[22]
Solid bases: alkaline earth metal oxides											
17	H_2O	120	calcined rehydrated HT, MgO, Amberlyst A21 ion exchanged resin, and commercial HTs[k]	MgO	36.4	25.1 (at 36.4% conv.)	n.d.	n.d.	no	n.d.	[9]
18	H_2O	90	Ca–Al mixed oxides	Ca–Al (3.0)[l]	87	38 (at 61% conv.)	Ca	n.d.	FT	heterogeneous	[29]
19	H_2O	160		CaO/ZrO_2	*ca.* 80	21 (at 30% conv.)	n.d.	n.d.	no	n.d.	[26]

			NaOH, TiO_2, ZrO_2, CaO/TiO_2, CaO/ZrO_2							
20	H_2O	120	MgO, supported MgO	MgO/Nb phosphate	65	24.6 (at 37% conv.)	Mg, P, Nb	n.d.	CT	ca. 30% homogeneous contribution	[24]
21	H_2O	90	MgO, natural MgO (CaO*MgO)	natural MgO (CaO*MgO)	48	33.4 (at 44.1% conv.)	Ca, Mg	n.d.	FT	heterogeneous	[30]
22	H_2O	95	MgO−ZrO_2, ZrO_2	$(MgO)_{0.76}(ZrO_2)_{0.24}$	50	33 (at 45% conv.)	Mg	n.d.	FT	mostly heterogeneous	[27]
23	H_2O[m]	90	MgO, Sn/ZSM-5, K/ZSM-5, Al_2O_3, SiO_2/Al_2O_3, ZrO_2/TiO_2, NaOH, $NaAlO_2$	MgO[n]	79	33.4 (at 44% conv.)	n.d.	n.d.	no	heterogeneous[o]	[8]
24	H_2O	100	MgO/biochar	Mg/biochar prepared by wood impregnation with $MgCl_2$ followed by pyrolysis	45	30 (at 38% conv.)	Mg	9−10	no	heterogeneous catalysis was more important than homogeneous[p]	[28]
25	H_2O	80	CaO/C	CaO/C	50	29.2 (at 41% conv.)	n.d.	n.d.	no	n.d.	[31]
Solid bases: other inorganic materials											
26	H_2O	100	titanosilicates, sodium yttrium silicate, alkali calcium silicate, calcium silicate	sodium yttrium silicate, calcium silicate	56	39 (at 48% conv.)	Na, K	n.d.	CT	heterogeneous	[48]
27	H_2O	200	TiO_2, ZrO_2	ZrO_2	n.d.	13 (at 50% conv.)	n.d.	n.d.	no	n.d.	[51]
28	H_2O	100	attapulgite (Mg silicate mineral)	attapulgite (Mg silicate mineral)	36.8	20.6 (at 26.4% conv.)	n.d.	n.d.	no	n.d.	[23]
29	H_2O	110	$SrTiO_3$, $BaTiO_3$, $CaTiO_3$, $Na_2Ti_6O_{13}$,$K_2Ti_6O_{13}$, and $Sr_3Ti_2O_7$	$SrTiO_3$, $CaTiO_3$, $Na_2Ti_6O_{13}$	47	32 (at 41−47% conv.)	Sr	n.d.	FT	heterogeneous	[32]
30	H_2O	100	Aveiro-Manchester material number 4 AM-4 (Na_3(Na, H) Ti_2O_2 $[Si_2O_6]_2$, $2H_2O$), AM-4 with different alkali and alkaline earth metals	Mg-AM-4	61	27 (at 39% conv.)	Na, K, Ca, Mg	n.d.	CT	heterogeneous with homogeneous contribution for Ca-AM-4, K-AM-4, and Na-AM-4; heterogeneous for Mg-AM-4	[25]
31	H_2O	80	element oxides (MgO, Al_2O_3, SiO_2, TiO_2, ZrO_2, Nb_2O_5, and CeO_2) treated with NH_3	ammonia treated SiO_2	40	ca. 36 (for 45% conv.)	nitrogen	n.d.	FT	a low contribution of dissolved species	[49]
32	H_2O	120	zirconium carbonate	zirconium carbonate	45	34 (at 45% conv.)	n.d.	n.d.	FT	heterogeneous	[50]
33	H_2O	100	mesoporous ordered molecular sieves of the M41S family, containing their organic template, zirconia promoted with Cs	M41S	ca. 23	18 (at ca. 23% conv.)	n.d.	n.d.	CT	n.d.	[52]
Soluble amines											
34	H_2O	100	morpholine, piperazine, ethylenediamine, trimethylamine, piperidine, and pyrrolidine	triethylamine	75	32 (at 51% conversion)	–	*ca.* 11 (pH_0)	–	homogeneous	[33]
35	H_2O	100	triethylamine	triethylamine	64 (max. conversion depends on the catalysts' concentration)	32 (at 50% conversion)	–	9.5−11.5 (pH_0)	–	homogeneous (hydroxide ions generated via interaction of the amine with water were proposed to be catalytically active species)	[34]
36	H_2O	100	quinuclidine, trimethylamine, diisopropylethylamine, tri-n-propylamine	quinuclidine	55	29 (at 43% conv.)	–	10.9−11.7	–	homogeneous	[35]
37	1 wt.% NaCl in H_2O	110	soluble PEI[q]	branched and comb PEI	58 (max. Glc conv. depends on PEI structure, temperature, and catalyst concentration)	34 (at 45% conv.)	–	10.2−11.7	–	homogeneous (hydroxide ions generated via interaction of the amine with water were assumed as catalytically active species)	[36]
38	H_2O	120	amino acids (arginine, lysine, and histidine)	arginine		31 (at 41% conv.)	–	10.2 (pH_0)	–	homogeneous (hydroxide ions generated via	[37]

Table 1. (*continued*)

					50 (max. Glc conv. depends temperature and catalyst concentration)					interaction of the amine with water were assumed as catalytically active species)	
39	D_2O	100	a large number of soluble and solid bases	meglumine	n.d.	35 (at 40% conv.)	–	10.4 (pD_0)	–	homogeneous	[38]
40	H_2O[r]	80	molecules mimicking Glc isomerase with carboxyl, amino, imidazole, and phenolic groups	BBTA (Figure 2b)	*ca.* 41	33 (at 35% conv.)	–	8.5	–	homogeneous	[43]
41	H_2O	100	amines onto C_{60} fullerenes	ethanolamine and diethyleneamine with a molar ratio of 1:3 grafted onto C_{60}	n.d.	19.5 ± 6.4 (at 29.0 ± 2.39% conv.)	n.d.	n.d.	–	hydroxide ions generated via interaction of the amine with water were assumed as catalytically active species	[39]
42	H_2O	70	basic ionic liquids	choline proline	62 (max. Glc conv. depends on temperature and catalyst concentration)	37.6 (at 48.7% conv.)	–	n.d.	–	homogeneous	[41]
43	H_2O	80	basic ionic liquids	tetrabutyl ammonium proline	68 (max. Glc conv. depends on temperature and catalyst concentration)	36.8 (at 50% conv.)	–	11.4	–	homogeneous	[42]
44	H_2O	80	IMD, API, TREN, PEI, TMG, TBD[q]	TMG (TBD showed similar results)	65 (max. Glc conv. depends on temperature)	33 (at 45% conv.)	–	8.0–11.2	–	homogeneous	[46]
45	H_2O	100	N-doped mesoporous carbon materials	the materials after hydrogenation treatment	45 (max. Glc conv. depends on temperature)	31.6 (at 37.4% conv.)	n.d.	n.d.	no	n.d.	[47]
46	1 wt.% NaCl in H_2O	80	polystyrene-supported organic bases (PS-TBD, PS-DBU, and PS-BEMP)[q]	PS-BEMP	70 (max. conversion depends on the catalysts concentration, temperature, and the presence of salts)	41 (at 58% conv.)	–	n.d.	–	homogeneous (hydroxide ions generated via interaction of the amine with water were assumed as catalytically active species)	[45]
Solid bases: nitrogen-containing materials											
47	H_2O	100	SBA-15 bearing grafted organosilanes with amino groups	(N,N-diisopropyl aminomethyl) triethoxysilane grafted on SBA-15	37	26 (at 32% conv.)	leaching of organosilanes	10	FT	heterogeneous with minor contribution of homogeneous	[35]
48	H_2O[s]	100	SBA-15 bearing grafted organosilanes with tertiary amine functionalities	material with high amine loading (~0.95 mmol g^{-1}) and methyl linker	ca. 30	23 (at 31% conv.)	leaching of organosilanes	9.1–6.8	no	n.d.	[44]
49	H_2O	120	PS-API PS-TMG PS-TBD (Merrifeld's peptide resin), magnetically separable, core–shell Fe_3O_4@SiO_2-amines (API, TMG, TBD)[q]	core–shell Fe_3O_4@SiO_2-amines	60 (max. Glc conv. depends on temperature and catalyst concentration)	25 (at 46% conv.)	nitrogen loss for PS-TMG	9.8–11.0 (pH_0)	no	n.d.	[46]
50	acetone:H_2O (1:1 v/v)[t]	160	biochar derived from spent coffee grounds and melamine	biochar derived from spent coffee grounds and melamine	22	19 (at 22% conv.)	no nitrogen leaching	8.24 (pH_0)	–	heterogeneous[u]	[40]
51	H_2O	110	branched PEI cross-linked with glutaraldehyde	branched PEI cross-linked with glutaraldehyde	n.d.	41 (at 55% conv.)	n.d.	n.d.	no	hydroxide ions generated via interaction of the amine with water were assumed as catalytically active species	[36]
Buffers											
52	H_2O	110	phosphate buffer Na_2HPO_4+NaH_2PO_4	phosphate buffer Na_2HPO_4+NaH_2PO_4	60	30 (at 51% conv.); max. Fru yield was 51% for extraction-assisted isomerization	–	7.5	–	homogeneous (specific base catalysis)	[57]
53	H_2O:EtOH (80:20 v/v)	63	carbonate buffer Na_2CO_3+$NaHCO_3$	carbonate buffer Na_2CO_3+$NaHCO_3$	70	29 (at 55% conv.); max. Fru yield was 56% for adsorption-assisted isomerization	–	10	–	homogeneous	[63]

[a] with regard to the highest Fru yield.

[b] test conducted by the authors to uncover contributions of homogeneous and heterogeneous catalysts, namely filtration test (FT) or contact test (CT). In FT, the catalyst is removed by filtration from the reaction medium, and the filtrate is allowed to react further; in CT, the catalyst is set in contact with a solvent under the reaction temperature, then the solid catalyst is filtered off, the substrate is dissolved in the filtrate, and is allowed to react.

[c] a conclusion drawn by the authors regarding the nature of catalysis.

[d] classical Langmuir–Hinshelwood mechanism is deduced.

[e] HT in hydroxide form also showed promising results.

[f] prepared by co-precipitation in aqueous medium at pH 10 or in aqueous–EtOH medium at pH 9.5.

[g] AMOST stands for aqueous miscible organic solvent treatment.

[h] NaX and KX were indicated by the authors as the best catalysts showing the highest selectivity for Fru, though the highest yield of 22% was obtained with CsA.

[i] MgK-zeotype catalyst showed the highest stability against leaching, whereas a somewhat higher Fru yield was obtained in the presence of CaK-DZSM-5.

[j] parent NaY zeolite was treated with 0.02 M NaOH.

[k] in a continuous flow reactor.

[l] mixed oxides with molar ratio of Ca to Al of 3.0.

[m] yields of Fru in DMSO, DMSO/H_2O mixture, DMA, DMA/H_2O mixture, and sulfolane/H_2O mixture were lower than in H_2O.

[n] MgO is the best solid catalyst; in the presence of $NaAlO_2$, 52.1% Fru yield was obtained.

[o] the authors proposed a mechanism including surface species.

[p] this conclusion was drawn by the authors based on the statistical analysis and on a stronger correlation of Fru yield with Mg content in the MgO-biochars than Mg concentration in solutions.

[q] the amines are abbreviated as follows: 1,8-diazabicyclo [5.4.0] undec-7-ene (DBU), 1,5,7-triazabicyclo [4.4.0] dec-5-ene (TBD), 2-tert-butylimino-2-diethylamino-1,3-dimethylperhydro-1,3,2-diazaphosphorine (BEMP), polyethylenimines (PEI), 1-(3-aminopropyl) imidazole (API), imidazole (IMD), and tris(2-aminoethyl)amine (TREN).

[r] Glc conversion in THF/H_2O, DMF/H_2O, and DMSO/H_2O mixtures was lower than in H_2O.

[s] Glc conversion in 50:50 water/ACN, water/EtOH, water/DMSO, and water/THF mixtures was lower than in water.

[t] reaction rate in acetone-water mixture was higher than in water.

[u] this conclusion was drawn by the authors based on the initial pH of the reaction mixture in H_2O of 7.24.

$$M(OH)_2 \rightleftharpoons M^{2+} + 2OH^- \quad (2)$$

$$\text{Zeolite}-O-M + H_2O \rightleftharpoons \text{Zeolite}-O-H + M^+ + OH^- \quad (3)$$

What are the roles played by homogeneously distributed OH^- species and surface basic sites? An answer to this question is still needed to be found. Interestingly, the pH values of the reaction mixtures are reported in the research papers very rarely, though OH^- is a well-known catalyst for the isomerization [1,2,5]. Leaching of metals during the reaction takes place literally for all the inorganic solid catalysts, and this leaching is accompanied with the formation of the hydroxide species (Eqs. (2) and (3)). Typically, a filtration test is utilized to access catalytic activity of the OH^- anions. Based on the results of this test, either no or a minor contribution of dissolved OH^- as catalyst was reported, and the catalysis was concluded to be (predominantly) heterogeneous [10,11,18–22,24,25,27,29,30,32,35,49,50,52]. Despite this, establishing correlations between textural properties of materials and their catalytic activity remains challenging [48]. Qi et al. monitored the isomerization of Glc in the presence of NaX zeolite using *operando* solid state NMR technique [54]. The authors distinguished the resonance signals corresponding to adsorbed and dissolved Glc, and observed the same rates of conversion for Glc in the catalyst pores and mobile Glc molecules in the solution phase. This was explained by a rapid exchange of these two populations on the time scale of the reaction.

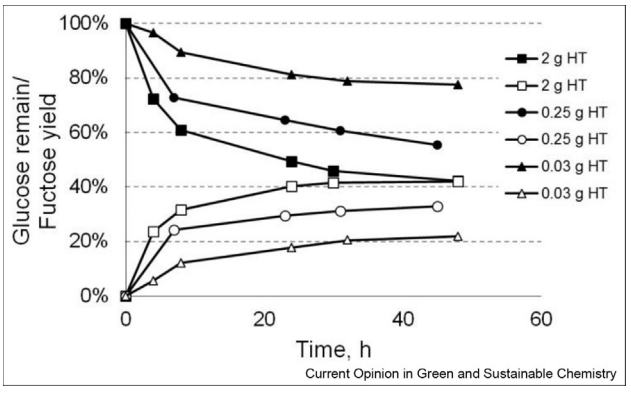
Basicity of the catalysts correlates rather well with the outcome of the isomerization reaction. Increasing the catalyst basicity leads to an enhanced initial rate of the isomerization [6,10,12,26,27]. In the presence of base catalysts, a full conversion of Glc is rarely observed; typically the reaction stops upon reaching a certain conversion value (Figures 1 and 2a)). The maximum conversion seems to increase upon enhancing catalyst basicity [27], amount of the catalyst [10,37,46], and temperature [37,45,46]. Delidovich and Palkovits addressed this phenomenon for Glc isomerization in the presence of Mg–Al hydrotalcites [10]. Adsorption of organic byproducts and partial neutralization of hydrotalcite were hypothesized as the reasons for the deactivation. An increase of the catalyst stability could be achieved under continuous conditions, i.e., upon a permanent withdrawal of the byproducts. Nevertheless, a rational design of a catalyst, which is stable under the reaction conditions, is still required.

A number of recent works focus on amines as commercially available organic bases with versatile structures. In general, the rate of Glc isomerization correlates with the basicity of the amines, i.e., with pK_a values of their conjugated acids [33]. Carraher et al. studied kinetics and mechanism of Glc isomerization in the presence of trimethylamine [34]. Based on the similarity of the apparent rate constants for the isomerization of Glc in the presence of triethylamine and NaOH, the authors concluded that the hydroxide ions generated in aqueous solutions (Eq. (1)) serve as catalytically active species. The latest results indicate though that the catalytic properties of some amines, such as rate of isomerization or conversion–selectivity curves, dramatically depend on their structure. Deshpande et al. reported that the initial reaction rate and a maximum Glc conversion significantly differ for trimethylamine, diisopropylethylamine, tri-n-propylamine, and quinuclidine, though these amines have similar basicity and pH values in their solutions (Figure 2a) [35]. Chen et al. recently screened a number of amines and reported an increased selectivity for Fru in the presence of some amines, for example, meglumine [38]. The authors hypothesized stabilization or destabilization of an enediol anion intermediate upon interaction with BH^+, a conjugated acid of the corresponding amines, which apparently promotes isomerization. A very impressive result was published by Zhang et al. who obtained Fru in yield of 33% with selectivity as high as 93.5% using 2,2′,2″,2‴-(((2-hydroxy-5-methyl-1,3-phenylene) bis (methylene))-bis(azanetriyl))tetraacetic acid (BBTA) as a catalyst (Figure 2b) [43]. BBTA was designed by the authors aiming at mimicking phosphoglucose isomerase, a glucose isomerase that catalyzes the interconversion of glucose 6-phosphate and fructose 6-phosphate. The isomerization in the presence of BBTA was efficient under very mild reaction conditions, 80°C and 4 h. The apparent activation energy of 65.9 kJ/mol observed in the presence of BBTA was far below the activation energy in the presence of NaOH (*ca.* 120 kJ/mol) [55]. Importantly, though the similar mechanism via enediol anion is generally accepted for the isomerization of Glc in the presence of amines, the apparent activation energies for catalysis by amines vary in a large range of 30–60 kJ/mol [34,36,37] and seem to depend on the structure of an amine.

Solid nitrogen-containing catalysts were synthesized for heterogeneous isomerization, e.g., by immobilization of the amines onto Merrifeld's peptide resin [45,46] or silica supports [35,44,46]. In both cases, an influence of support–amine interaction onto the catalytic activity appeared to be significant. Deactivation of catalysts due to the leaching of grafted amines from silica support [35,44] and adsorption of side products onto the resins [46] were reported. Other strategies of heterogenization of the amines include synthesis of cross-linked polyethylenimines [36] or utilization of nitrogen-decorated carbon [40,47].

Very promising results were recently obtained with hydrotalcites as catalysts using alcohols as solvents. The yields of Fru were 56% and 51% in ethanol [15] and 1-butanol [16], respectively. Acceleration of the isomerization reaction in alcohols compared to aqueous medium can be explained by greater ionization constants of saccharides in alcohols [56]. Interestingly, selectivity for Fru in alcohols depends on the composition of the applied catalyst, and the best results were reported for hydrotalcite in carbonate form [15,16].

Figure 1

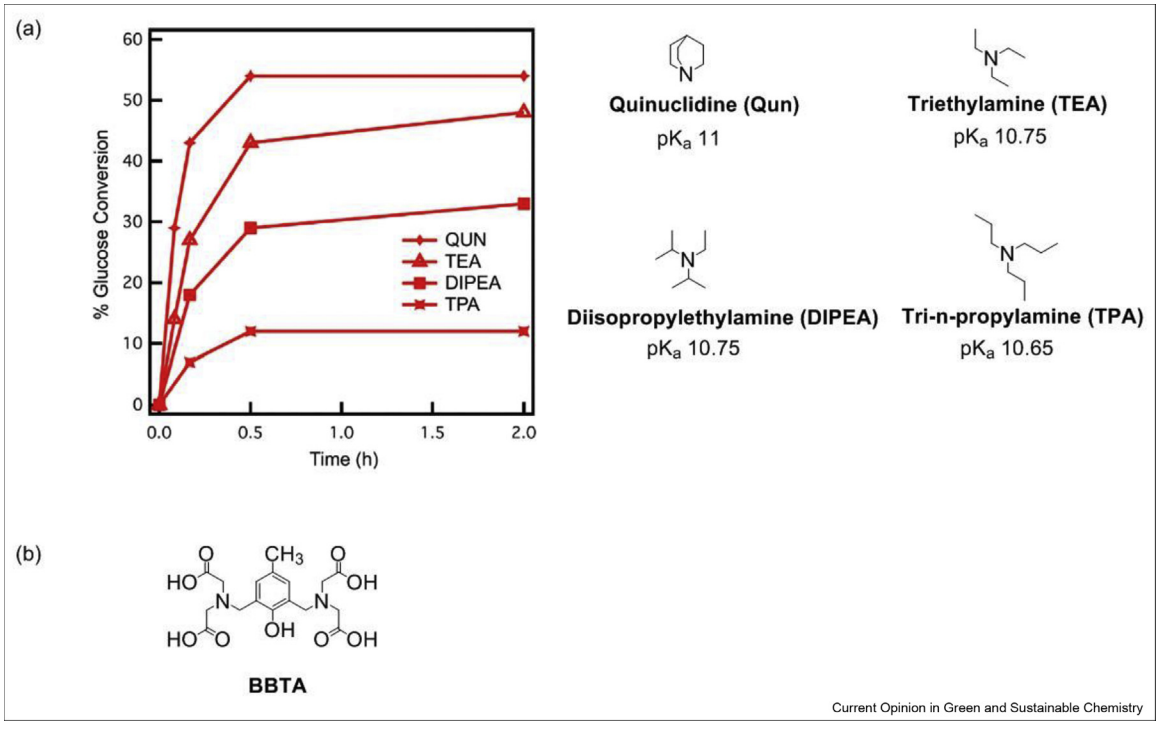


Isomerization of Glc into Fru under batch conditions in the presence of Mg–Al hydrotalcite (HT). Increase of the catalyst mass results in the enhanced initial isomerization rate as well as in the maximal product yield. Reproduced from Refs. [10] with permission from The Royal Society of Chemistry.

Buffer solutions present another type of catalysts for isomerization of saccharides. Delidovich and Palkovits demonstrated an efficiency of the phosphate buffer NaH_2PO_4+Na_2HPO_4 at pH 7.5 for the isomerization of Glc [57]. This catalyst was also applied for isomerization of other aldoses into ketoses [58–61]. Specific base catalysis in the presence of phosphates was observed, indicating OH^- ions as catalytically active species [57]. Interestingly, a dependence of catalytic activity on the nature of buffer was recently reported for isomerization of D-galactose, another biomass-derived aldose [59]. This result does not corroborate with a conclusion on a specific base catalysis, for which a dependence of the reaction rate on the nature of buffer is not expected. Thus, a deeper insight into reaction mechanism of isomerization of saccharides by buffers and its comparison with other base catalysts is required.

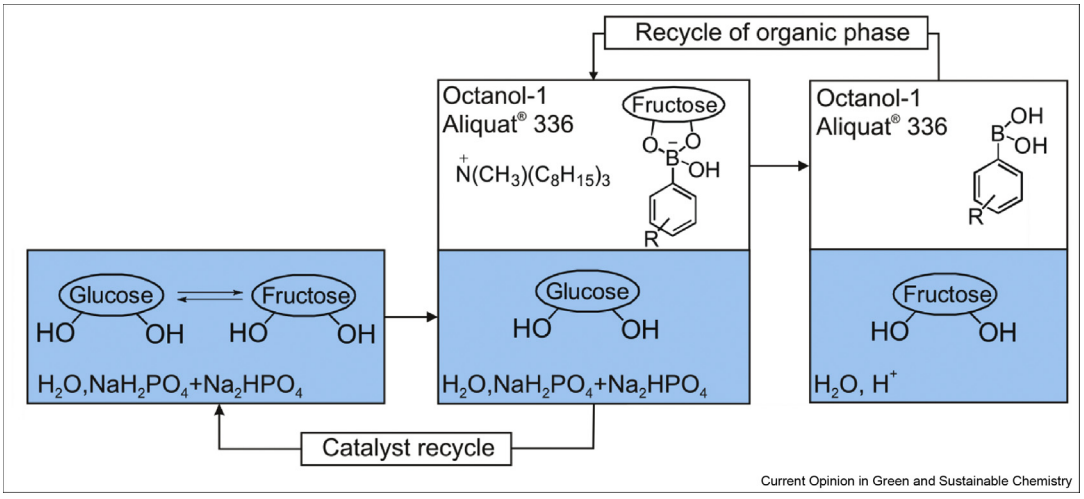
The isomerization in buffer solutions at basic pH values can be readily coupled with recovery of Fru using a principle of "molecular recognition" [62]. This approach is based on a preferable complexation of phenylboronic acids with Fru even in the presence of its isomer Glc, i.e., a phenylylboronic acid "recognizes" Fru. Delidovich and Palkovits proposed a recovery of Fru using anionic extraction into an organic medium comprised of a phenylboronic acid, Aliquat 336® as a quaternary amine anion for charge balancing of the anionic complex, and 1-octanol as a diluent (Figure 3) [57]. After extraction of Fru, the aqueous phase containing Glc and phosphates can be re-used for catalysis. Fru can be back-extracted into acidified aqueous medium. Schroer et al. proposed adsorption of Fru instead of extraction, using cross-linked functionalized polymers bearing phenylboronate moieties [63].

Figure 2



Amines used for isomerization of Glc into Fru. (a) Isomerization of Glc into Fru under batch conditions in the presence of amines of similar structure and basicity, the formulae of the amines and pK_a of their conjugate acids [35]. Reproduced with permission from Elsevier. (b) The chemical structure of BBTA [43]. Reproduced with permission from John Wiley and Sons.

Figure 3



Isomerization of Glc into Fru coupled with a product recovery via anionic extraction. Reproduced from Refs. [57] with permission from The Royal Society of Chemistry.

Adsorption procedure does not require utilization of an organic diluent or Aliquat 336®, improving an environmental impact of this separation strategy. Importantly, CO_2 can be used for desorption of Fru, i.e., no molecular acids are required. Isomerization of Glc into Fru in carbonate buffer was successfully coupled with Fru adsorption. Nevertheless, the proposed cross-linked polymers suffer from relatively slow adsorption accompanied with significant swelling of the materials, which complicates the continuous adsorption. Thus, despite the obtained proof-of-concept for the separation of Fru via adsorption, further improvement of material structure is required.

In summary, a number of promising directions for development of base-catalyzed Glc-Fru isomerization processes have been recently identified. For catalysis by inorganic materials, the questions on relationships between structure of materials and their stability, as well as the nature of catalytically active species, remain open. Recent results indicate that a potential contribution of general base catalysis into catalysis by amines and buffers cannot be excluded. Moreover, tailoring the structure of the catalyst along with the reaction conditions—especially utilization of alcohols as solvents seems to be promising—enables reaching outstanding yields of Fru. The obtained results build a solid basis for the future work aimed at development of a more stable and selective catalyst coupled with a facile product separation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.cogsc.2020.100414.

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