Glucose to Value-added Chemicals: Anhydroglucose Formation by Selective Dehydration over Solid Acid Catalysts

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Selective dehydration of glucose to anhydroglucoses, 1,6-anhydro-β-D-glucopyranose (levoglucosan) and 1,6-anhydro-β-D-glucofuranose, which are highly value-added intermediates for drugs, polymers, and surfactants was performed. Solid acids with sulfonic acid groups like Amberlyst-15 were found to effectively produce anhydroglucoses in polar aprotic solvents.

Production of chemicals such as solvents, surfactants, polymers, cosmetics, and pharmaceuticals deeply rely on petroleum resources. They should be however, synthesized from renewable resources from the viewpoint of severe global warming. The concept of carbon-neutral allows us to utilize biomass as a nonpetroleum candidate to overcome this problem.[1] Among biomass utilization, cellulose conversion from wood including gasification and hydrolysis has attracted considerable attention because of the nonfood nature and universal availability.[2–4] Glucose, which is produced by hydrolysis of cellulose, is further transformed into ethanol as biofuel by fermentation, 5-(hydroxymethyl)furfural and sorbitol as chemical intermediates by catalytic processes.

Dehydration of glucose gives two products, 5-(hydroxymethyl)furfural and anhydroglucose as shown in Figure 1; the former is obtained by removal of three water molecules and the latter is by one water. Little has been reported about the formation of anhydroglucose, though anhydroglucose is a highly value-added chemical for drugs, surfactants, and polymers,[5] e.g., ring-opening polymerization of anhydrosugars results in the formation of hyperbranched polysaccharides with spherical macromolecular structure.[6]

Anhydroglucose has been obtained by tosylation of glucose and successive neutralization by sodium hydroxide,[7] pyrolysis of starch or cellulosic biomass,[8] and noncatalytic dehydration from glucose at high temperatures, typically above 573 K.[9] Here we demonstrate efficient production of anhydroglucose by selective dehydration of glucose over solid acid catalysts under mild conditions. Solid acid catalysts offer the opportunity to reduce environmental impact because of easy separation from product, nontoxicity, and reusability.

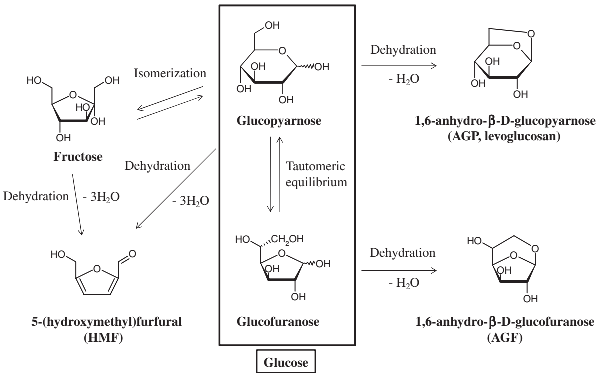

Figure 1. A reaction scheme for glucose transformation.

A general reaction scheme for glucose transformation according to the literature[9] is shown in Figure 1. 1,6-Anhydro-β-D-glucopyranose (AGP, levoglucosan) and 1,6-anhydro-β-D-glucofuranose (AGF) were formed by intramolecular dehydration of glucopyranose and glucofuranose, respectively, where pyranose and furanose forms are under tautomeric equilibrium.

The reaction was performed using 0.1 g of solid acid catalyst, 0.1 g of glucose and 3 mL of solvent at 373–393 K.[10] The typical results of dehydration of glucose in *N*,*N*-dimethylformamide (DMF) over several solid acid catalysts at 373 K for 3 h are listed in Table 1. Ion-exchange resins, metal oxides, clay, and H-type zeolites were used as solid acid catalysts.

Amberlyst-15 which is a styrene–divinylbenzene sulfonated ion-exchange resin was found to produce anhydroglucoses, AGP and AGF; high conversion and selectivity were achieved at 393 K. Nafion NR50, a perfluorinated resin sulfonic acid also exhibits moderate activity for selective dehydration of glucose with high selectivity. Other conventional solid acids such as niobic acid, SO_4/ZrO_2, H-montmorillonite, and H-type zeolites (HZSM-5 and HY) were inactive for the reaction. Under the above conditions, fructose by isomerization and HMF by elimination of three water molecules were not obtained in any case. This selective dehydration also proceeded in other polar aprotic solvents which can dissolve glucose such as dimethyl sulfoxide, 1,3-dimethyl-2-imidazolidinone, *N*-methylpyrrolidone, and sulfolane at comparable yields to that in DMF.[10]

Table 1. Anhydroglucose formation from D-glucose over solid acids[a]

Catalyst	Conversion /%	Yield/% (Selectivity/%)		
		AGP[b]	AGF[c]	AGP + AGF
Amberlyst-15	69	15	17	32 (47)
	88[d]	33[d]	30[d]	63 (71)[d]
Nafion NR50	34	12	14	26 (77)
SO_4/ZrO_2[e]	7	0	0	0
$Nb_2O_5 \cdot nH_2O$	12	0	0	0
TiO_2	2	0	0	0
H-Mont	6	0	0	0
HZSM-5[f]	2	0	0	0
HY[g]	4	0	0	0
Blank	2	0	0	0

[a] Reaction conditions: glucose (0.1 g), catalyst (0.1 g), DMF (3 mL), 373 K, 3 h. [b] 1,6-Anhydro-β-D-glucopyranose. [c] 1,6-Anhydro-β-D-glucofuranose. [d] 393 K. [e] From Wako Pure Chemicals. [f] JRC-Z5-90H. [g] JRC-Z-HY5.5.

Table 2. Anhydroglucose formation from D-glucose over solid and liquid sulfonic acids[a]

Catalyst[b]	Reaction temp/K	Conv. /%	Yield/% (Selectivity/%)		
			AGP	AGF	AGP + AGF
Amberlyst-15	373	28	14	14	28 (>99)
	393	66	25	22	46 (70)
Nafion NR50	373	36	13	14	26 (75)
	393	58	15	17	32 (56)
Nafion SAC13	373	25	12	11	24 (96)
	393	71	13	17	30 (43)
p-TsOH	373	60	15	16	31 (52)
H_2SO_4	373	57	13	15	29 (51)

[a]Reaction conditions: mole ratio of acid amount of catalyst:glucose:DMF = 1:3:250. 3 h. [b]Acid amounts of samples tested are 4.8, 0.9, 0.15, 5.3, and 20.4 mmol g^{-1} for Amberlyst-15, Nafion NR50, Nafion SAC13, *p*-TsOH, and H_2SO_4, respectively.

Table 2 shows anhydroglucose formation over sulfonated solid acids, *p*-toluenesulfonic acid and concentrated sulfuric acid under a molar ratio of acid catalyst (SO_3H groups), glucose, and DMF of 1:3:250. At 373 K, yields of anhydroglucoses were almost the same among solid and liquid acids tested. It should be noted that Amberlyst-15 and Nafion SAC13, which is a highly dispersed Nafion on amorphous silica, exhibit excellent selectivity of anhydroglucoses (above 95%), whereas the selectivity for *p*-TsOH and H_2SO_4 was about 50%. At 393 K, yields of anhydroglucoses increased for Amberlyst-15 with high selectivity (70%) even at glucose conversion of 66% comparable conversion for liquid acids at 373 K. However, anhydroglucoses yields for Nafion NR50 and Nafion SAC13 did not improve with increasing reaction temperature, resulting in low selectivity. The resultant solution was yellow-brown and contained furan compounds as detected by GC-MS analysis. This suggests that undesired by-products might be furan-derived oligomers which were formed by acid-catalyzed reactions. Glucose is known to be polymerized and/or carbonized by concentrated sulfuric acid ca. 373 K, and this behavior is used for porous carbon materials.[11] From these results, it is thought that relatively weak acidity of Amberlyst-15 ($H_0 = -2.2$)[12] affords high selectivity whereas strong acidity of Nafion ($H_0 \leq -12$)[13] causes undesired oligomers. The reaction mechanism over SO_3H-bearing resins is considered as in the case of *p*-TsOH where the primary hydroxy groups (C-6) of glucose was selectively tosylated.[7] Such reactions seem to be performed over SO_3H-bearing ion-exchange resins.

Time courses of glucose dehydration over Amberlyst-15 at 373 and 393 K are shown in Figure 2. At 373 K, considerably high selectivity of anhydroglucoses (>99%) was obtained over 1–3 h. At 393 K, significant increase of yields as well as conversion was observed at the initial time. After three hours, however, anhydroglucoses yields did not change, suggesting that produced water inhibits the dehydration because this reaction did not proceed in water.[10] Further investigation is therefore necessary to improve the reaction system such as flow reactor system to remove water continuously and develop solid acids with a high density of SO_3H groups in order to obtain anhydroglucoses with high yield and selectivity.

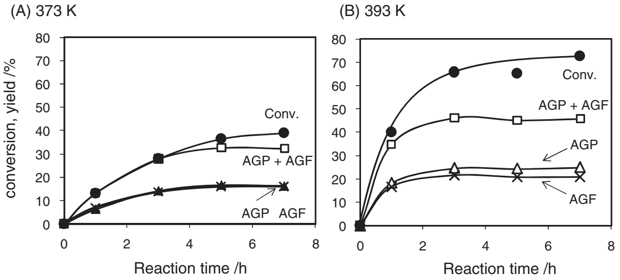

Figure 2. Time courses of glucose dehydration into anhydroglucoses over Amberlyst-15 at (A) 373 and (B) 393 K. glucose conversion (●), yields of anhydroglucoses (AGP + AGF) (□), yield of AGP (▲), and AGF (×). Reaction conditions: Glucose (0.432 mmol), Amberlyst-15 (30 mg, acid amount; 0.144 mmol), and DMF (36 mmol).

In summary, selective dehydration of glucose into anhydroglucoses over solid acids with sulfonic acid groups was performed under mild conditions. Amberlyst-15 was found to exhibit remarkably higher selectivity of anhydroglucoses at high conversions than Nafion and sulfuric acid due to relatively weak acidity.

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