



REVIEW

Chemical Isomerization of Glucose to Fructose Production

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Efficient chemical catalyst is becoming a research hotspot in isomerization of glucose to fructose, because the chemical catalyst rather than enzyme has a wider operating temperature range, a longer lifetime and a higher resistance to impurities. The most commonly used chemical catalysts for isomerization of glucose to fructose can be divided into five principal groups, such as homogeneous bases, heterogeneous bases, Lewis acids, aluminates and subcritical water. Thus, the focus of this review is mainly on isomerization of glucose to fructose by using chemical catalysts and mechanistic aspects of the isomerization reaction in order to gather maximum information in one manuscript for a better comprehension of the technological characteristics and specificities of fructose synthesis.

Keywords: Glucose, Fructose, Isomerization, Chemical catalyst.

INTRODUCTION

Fructose is widely used in the food industry, for example, a sweetener (high-fructose corn syrup, HFCS), since it contributes many useful physical and functional attributes to food and beverage applications, including sweetness, flavor enhancement, humectation, color and flavor development, freezing-point depression and osmotic stability^{1,2}. The isomerization of glucose to fructose for the production of HFCS has become the largest immobilized biocatalytic process worldwide³.

In addition, the recent drive to use biomass as an alternative to petroleum for the production of fuels and chemical intermediates has triggered renewed interests in carbohydrate chemistry. 5-Hydroxymethylfurfural (HMF) is a biobased platform chemical with high potential, which serves as a starting material for a wide variety of biobased chemical intermediates (e.g., levulinic acid, furandicarboxylic acid, dimethyl furan, γ -valerolactone and dihydroxymethylfuran)⁴⁻⁷. 5-Hydroxymethylfurfural is preferentially synthesized by dehydration of monosaccharides. Moreover, glucose is the most widely available hexose but its dehydration into HMF is known to occur at a slower rate compared to the dehydration of fructose, a ketohexose⁴. Consequently, the isomerization of glucose to fructose appears to be an important step for the efficient formation of HMF.

Currently, the reversible isomerization of glucose to fructose is carried out in large scale industrial processes in aqueous

phase with the immobilized enzyme D-glucose/xylose isomerase (D-xylose ketol isomerase; EC 5.3.1.5), which possesses high reaction specificity under benign pH conditions and relatively low reaction temperature. This reaction generates an equilibrium mixture of 42 wt. % fructose, 50 wt. % glucose and 8 wt. % other saccharides at a temperature of 318 K. The enzymatic process is highly selective, but it has several drawbacks that increase processing costs, including the slow process of enzymatic reactions, the use of buffering solutions to maintain pH, narrow operating temperatures, strict feed purification requirements and periodic replacement of the enzyme due to irreversible deactivation⁸.

The efficient chemical process using chemical catalyst has many advantages over the biological process for glucose isomerization, because the chemical catalyst rather than enzyme has a wider operating temperature range, a longer lifetime and a higher resistance to impurities.

A large number of reagents have good performance in the isomerization of glucose to fructose, but the ideal chemical catalyst has not been found yet for the isomerization of glucose to fructose. This chemical catalyst must meet some important criteria, which are enumerated as follows⁹: (1) It must guarantee a maximum level of isomerization with a minimum of reaction by-products. (2) To be environmentally safe and not toxic. (3) The cost of the catalyst must be as low as possible. (4) To be available in great quantity. (5) It must be easy to remove from the medium by traditional demineralization tools. (6) To give repetitive results of isomerization.

However, in practice, the chemical catalysts used for the isomerization of glucose to fructose present positive and negative aspects.

The present review focuses on various issues related to the isomerization of glucose to fructose with a descriptive illustration on results obtained by using chemical catalysts. Systematic analysis of the most used chemical catalysts for the isomerization of glucose to fructose can be divided into several principal groups. They are homogeneous bases, heterogeneous bases, Lewis acids, aluminates and subcritical water. Attentions are also paid in discussing the mechanistic aspects of the isomerization reaction by different chemical catalysts in order to bridge the gap in understanding the factors responsible for selective conversion and selection of catalyst.

Isomerization of glucose by homogeneous base catalysts: Isomerization of aldoses to ketose by the action of aqueous inorganic bases such as $\text{Ca}(\text{OH})_2$, NaOH and KOH is well known. This isomerization reaction in homogeneous phase is called the "Lobry de Bruyn-Alberda van Ekenstein transposition" according to the name of the inventors¹⁰⁻¹³. The yields of fructose from base-catalyzed isomerization of glucose were only about 20-30 % and the selectivity of fructose was shown to be strongly dependent on the duration, basicity and the temperature of the reaction¹⁴⁻¹⁹. Tetramethylguanidine (TMG), as an organic base, was also reported to have catalytic activity in aqueous solution for glucose isomerization. The results showed that a maximum 37 % yield of fructose was obtained at 373 K with TMG to glucose molar ratio range of 0.06-0.25¹⁹.

Furthermore, the adding of additives has considerable effects on the aldose-ketose interconversion. Mendicino²⁰

reported that the presence of sodium borate led to the yield of fructose as high as 80-85 % in alkali-catalyzed isomerization. Barker *et al.*²¹ showed that the maximum yield of fructose was as high as 50 % in a process with isomerizing the glucose in an alkaline solution containing an aryl boric acid. Alcohol additives were reported to accelerate markedly the isomerization of glucose to fructose and *vice versa*. Specially, their rates in 70 % ethanol solution were 2.4 and 1.7 times the corresponding values in water solution¹⁶. However, alcohol additives did not play a key role in the yield of fructose¹⁹.

Studies using deuterated solvents showed that the mechanism of base catalyzed aldose-ketose isomerization involved proton transfer from C-2 to C-1 and from O-2 to O-1 of an α -hydroxy aldehyde to create the related α -hydroxy ketone, as illustrated in Fig. 1¹².

Despite the use of inexpensive catalysts, these homogeneous processes cause unavoidable problems with corrosion of reactors, separation and recycling of the catalyst, high costs for waste disposal and waste water treatment. At the end of reactions, the catalysts should be neutralized to form metal salts in most cases and a large amount of by-products are produced. Moreover, strong-base catalyzed interconversion of glucose and fructose is accompanied by side reactions that are often undesirable and which lead to various amounts of organic acids (such as metasaccharinic acid), colored substances of unknown structure, small amounts of reductones and traces of sugars that arise either from carbonyl migration or from dealdolization with subsequent recombination of fragments. These side reactions give low yields and require complex steps in order to remove degradation products^{12,13,17}.

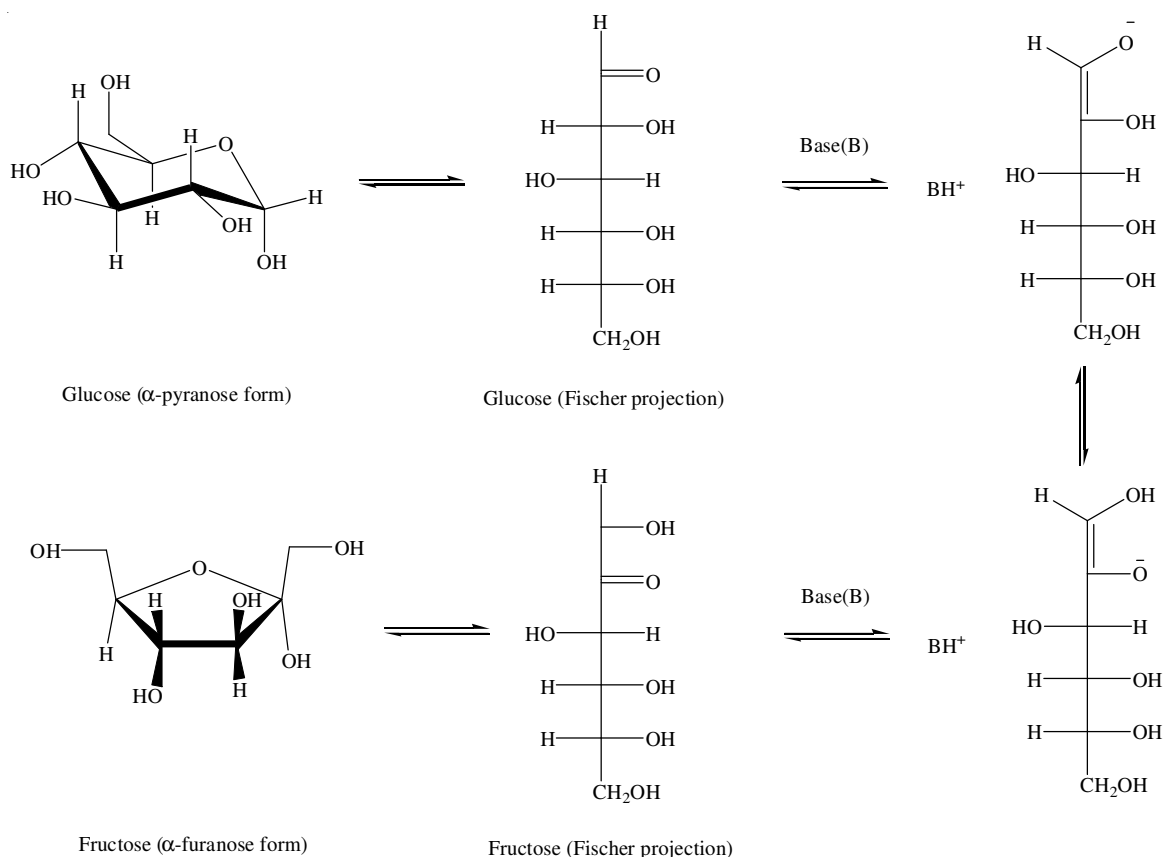


Fig. 1. Schematic representation of the glucose isomerization mechanisms by way of base-catalyzed

Isomerization of glucose by heterogeneous base catalyst:

Due to the drawbacks of homogeneous bases, the use of solid base catalysts in organic synthesis is expanding. Solid bases are easier to dispose than liquid bases. Meanwhile, separation and recovery of products, catalysts and solvents are less difficult and they are non-corrosive. The importance of the search for alternative heterogeneous alkali catalysts has come to be recognized for their environmentally benign qualities. So far, zeolites, hydrotalcites and anion exchange resins have been reported to have the activity in isomerization of glucose to fructose as solid base catalysts.

Zeolites and zeotype materials: Zeolites are microporous crystalline solids with well-defined structures. Generally they contain silicon, aluminium and oxygen in their framework and cations, water and/or other molecules within their pores. Zeolites simultaneously have acid and basic sites. Therefore, zeolites have the ability to act as catalysts for chemical reactions which take place within the internal cavities. They are often referred to as molecular sieves.

Alkaline cation-exchanged zeolites, such as Na-A, Na-X and Na-Y zeolites, were found to achieve isomerization of glucose to fructose in aqueous media in a batch mode. Those with a moderate basicity, such as Na⁺ and K⁺ exchanged X zeolites, achieved isomerization of glucose to fructose with the selectivity of fructose to about 90 %, but only 10-20 % glucose conversion. However, the high selectivity of fructose was only obtained at glucose conversions lower than 25 %. The optimized operating conditions were water as the solvent, at 368 K, up to 250 g/L of initial glucose concentration, up to 20 wt. % of catalyst based on the glucose amount, 700-1200 rpm and 8 bar of nitrogen pressure to avoid oxidation reactions^{22,23}. However, one major drawback when using cation-exchanged zeolites, particularly those containing monovalent cations such as Li⁺, Na⁺, K⁺ or Cs⁺, is a lixiviation phenomenon which leads to the formation of caustic effluents, even if this phenomenon tends to be stabilized with time on stream.

Several synthesized metallosilicate materials were also studied as solid base catalysts for the aqueous phase isomerization of glucose to fructose at 373 K. The reaction mixtures composed of 50 mg glucose, 20 mg powdered catalyst and 1 mL H₂O were stirred at 600 rpm for 2 h. The catalytic results obtained for the titanosilicate ETS-10 and the sodium yttrium silicate analogue of the mineral montregianite AV-1 in a first batch-run were similar to that observed for Na-X zeolite (20-25 % fructose yield). Characterized by Knoevenagel condensation (KC) test, the basicity of the titanosilicate ETS-4 was the highest, which was consistent with the measured fructose yields (39 %). This might be one reason why ETS-4 gave rise to the highest fructose yield despite its relatively low-specific surface area. Depending on the nature of the zeolites, catalyst deactivation could be explained by several factors, such as loss of crystallinity, sodium/potassium leaching and surface passivation²⁴.

As-synthesised mesoporous ordered molecular sieves of the M41S family, containing their organic template and used without any pretreatment, were shown to be efficient weak basic catalysts in glucose-fructose isomerization in a batch mode. Selectivities higher than 80 % were obtained for glucose conversion higher than 20 %. The batch catalytic reaction

conditions were that 1 wt. % of glucose solution was mixed with 5 wt. % basic hybrid catalyst based on the sugar amount under 20 bar of helium at 373 K for 2 h¹⁸. The superiority of the hybrid organic bases compared to the inorganic stronger solid base is correlated to the presence of a high number of weak basic sites intermediate between chemisorption and physisorption, resistant towards irreversible CO₂ poisoning. However, the recyclability of the catalyst was not studied.

A layered zirconium silicate, as a zeotype material, composed of SiO₄ tetrahedra and ZrO₆ octahedra, was hydrothermally synthesized in the presence of tetramethylammonium hydroxide (TMAOH) under relatively mild conditions in a wide range of Si/Zr and TMA/Si ratios. The novel layered zirconosilicate SZS had a high activity in the isomerization of glucose to fructose in water and could be reused²⁵. When the reaction mixture consisted of 150 mg glucose, 60 mg powdered SZS catalyst and 3 mL H₂O was kept at 373 K for 30 min, the conversion of glucose was 60 % glucose with yields of 26 % for fructose. These results were very similar to those obtained for Sn-β, a Lewis acid catalyst (fructose yield of 29 % after 0.5 h at 383 K)²⁶. The catalyst SZS had a lower activity after the first recycle. After three recycles, the fructose yield maintained the same value as after the first recycle while the fructose selectivity had increased from 51 to 76 %.

Commercial large-pore zeolites, such as H-Y, H-USY and H-β zeolites, were demonstrated to provide excellent catalytic performance in the isomerization of glucose to fructose in alcohol and aqueous media in two reaction steps. The novel reaction pathway involved glucose isomerization to fructose and subsequent reaction with methanol to form methyl fructoside (step 1), followed by hydrolysis to reform fructose after water addition (step 2), as illustrated in Fig. 2. The best result for formation of fructose was obtained by using the H-USY zeolite with optimal levels and distribution of Brønsted and Lewis acidity (Si/Al ratio = 6). Using this catalyst, it proved possible to maintain a high fructose yield of 50-55 %, with remaining 30-40 % glucose even with low catalyst loading (glucose-to-catalyst mass ratio = 12.5:1) at 393 K for prolonged reaction time²⁷. The main advantage of applying alcohol media and a catalyst with combining Brønsted and Lewis acid sites is that sugar isomerization is favored at low temperatures, while direct conversion to industrially important chemicals like alkyl levulinates is viable at higher temperatures.

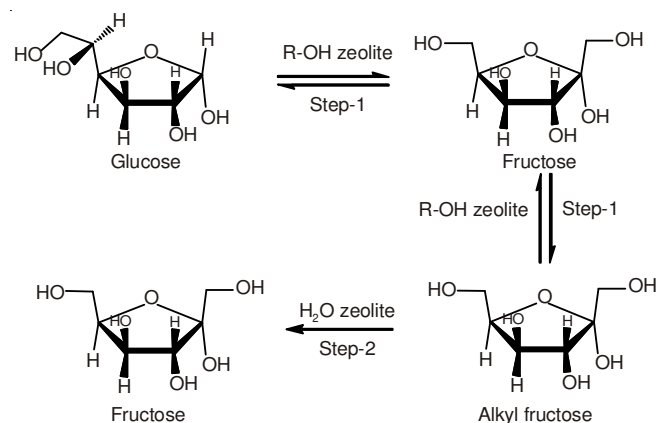


Fig. 2. Reaction pathway for isomerization of glucose to fructose over zeolites in alcohol and aqueous media

Hydrotalcites: Hydrotalcites, which are one of the layered double hydroxides (LDH), have been widely employed as efficient catalysts for various base-catalyzed reactions²⁸⁻³⁰. For this reason, their use as solid base catalysts of glucose isomerization reaction to fructose attracted considerable attention in the last decade.

Isomerization of glucose to fructose was easily performed in the presence of a commercial hydrotalcite catalyst, namely DHT-4A2 from Kyowa, in its carbonate, hydroxide or mixed carbonate-hydroxide form and in water as the solvent. Isomerization was readily achieved at 363 K in the presence of the DHT-4A2 catalyst, calcined at 673 K and rehydroxylated and with glucose to catalyst ratio between 2.5 and 5 wt. %. Under such conditions, the selectivity towards fructose was higher than 90 % up to 15 % of glucose conversion at 20-25 min of reaction time. The recycled catalyst was as active as a fresh sample and the selectivity towards fructose was unchanged³¹.

Isomerization of glucose to fructose was also carried out over as-synthesized Mg-Al hydrotalcite (HT_A), calcined Mg-Al hydrotalcite (HT_C) and rehydrated Mg-Al hydrotalcite (HT_R) catalysts with a ratio of Mg/Al = 3. Yield for fructose was up to 35 % when the catalytic reaction with HT_R (32 wt. % compared to glucose amount) in dimethylformamide was carried out at 353 K for 3 h. HT_R catalyst retained abundant weak base sites through exfoliation and vertical breaking of layers in the hydrotalcite structure during the rehydration process, leading to the enhanced catalytic performance of HT_R in this reaction. Reaction temperature and time served as a crucial factor determining the catalytic performance of hydrotalcite in the isomerization of glucose to fructose³². It is worth to note that the use of organic solvents instead of water is a possibility of providing fructose source that can be directly used without any purification in a 5-hydroxymethylfurfural process³³.

Takagaki *et al.*³⁴⁻³⁶ found that a combination of solid acid and base catalysts successfully afforded direct synthesis of 2,5-diformylfuran (DFF) and 5-hydroxymethylfurfural (HMF) from saccharides under mild conditions in one pot. In these simple one-pot reactions, Mg-Al hydrotalcite was also used as solid base catalysts for isomerization of glucose to fructose.

Anion exchange resins: Ion exchange resins can be used as a catalyst for almost all reactions catalyzed by acids or bases³⁷. Anion exchange resins can be used to intensify process isomerization of glucose to fructose by exploiting OH⁻ ions exchange between solution in reaction and resins and to simplify fructose production process by using the same resins for demineralization of the end product. The heterogeneous catalytic reaction of carbohydrates on a strongly alkaline ion exchanger can be described as taking place in a pseudo-homogeneous solution within the catalyst³⁸.

Langlois and Larson³⁹ reported a maximum yield of about 32 % for fructose from glucose on hydroxide form anion exchange resin at 360 K when the initial glucose concentration was 18-20 %. The final solution obtained was free of saccharinic acids, was very sweet, had no objectionable flavor and was water clear. However, the hydroxide form resin slowly lost its basicity due to the absorption of acids. Based on the reduction in acid absorptive capacity of the resin, it was calculated that the glucose lost by conversion to acids during the intercon-

version treatment was between 8 to 12.5 %. By forming a complex with fructose, resin-bound aluminate ion stabilized the fructose and permitted high yields (up to 72 %) of fructose from glucose. Moreover, lower temperatures gave the higher fructose yields but needed more reaction time⁴⁰.

The isomerization process using anion exchange resins as catalyst has some advantages as follows: (1) Demineralization stage is not needed; (2) there is no additional operation to purify the end product from dyes; (3) The process is more profitable in comparison with traditional enzyme methods. However, disadvantages of ion-exchange resin as catalyst are hydrothermal instability and difficult to regenerate^{37,41}.

Isomerization of glucose by heterogeneous Lewis acid catalyst: The isomerization of glucose to fructose could be catalyzed in aqueous media by hydrophobic zeolites that contain Lewis acids. Specially, large-pore pure-silica zeolites with the zeolite β -structure containing small amounts of framework Ti⁴⁺ or Sn⁴⁺ (denoted as Ti- β and Sn- β , respectively) were able to isomerize glucose to fructose in high yield at relatively low temperatures (383-413 K). The Sn- β sample had superior activity to the Ti- β material and could even convert higher concentration of glucose solutions. Specifically, a 10 wt. % glucose solution containing a low catalytic amount of Sn- β (1:50 Sn:glucose molar ratio) gave product yields of approximately 46 wt. % glucose, 31 wt. % fructose and 9 wt. % mannose after 30 min and 12 min of reaction at 383 K and 413 K, respectively. This reactivity was also achieved when a 45 wt. % glucose solution was used. Moreover, the Sn- β catalyst could be used for multiple cycles and the reaction stopped when the solid was removed, clearly indicating that the catalysis was occurring heterogeneously. Most importantly, the Sn- β catalyst was able to perform the isomerization reaction in highly acidic, aqueous environments with equivalent activity and product distribution as in media without added acid²⁶. This enables Sn- β to couple isomerizations with other acid-catalyzed reactions, including hydrolysis/isomerization (starch to fructose) or isomerization/dehydration (glucose to HMF) reaction sequences^{42,43}.

The isomerization reaction mechanism with Sn- β (and to a great extent Ti- β) is very similar to that of the metalloenzyme D-xylose isomerase^{44,45}. As shown in Fig. 3, glucose partitions into the zeolite in the pyranose form, ring opens to the acyclic form in the presence of the Lewis acid center, isomerizes into the acyclic form of fructose and finally ring closes to yield the furanose product⁴⁶. The Sn- β catalyzed isomerization reaction of glucose to fructose in water takes place by way of an intramolecular hydride shift, using ¹H and ¹³C NMR spectroscopy on isotopically labeled glucose. Although Lewis acidity is usually suppressed by the presence of water, verification of this mechanistic pathway confirms that framework Sn sites within the hydrophobic pores of Sn- β act as Lewis acids in aqueous media. There is also further research suggesting that extra framework Sn sites located within the hydrophobic channels of zeolite β can isomerize glucose to fructose in water, but through a base-catalyzed proton-transfer mechanism. However, SnO₂ particles located at external zeolite crystal surfaces or supported on amorphous silica do not catalyze isomerization in water, suggesting that contact with bulk water inhibits isomerization at SnO₂ surfaces^{47,48}.

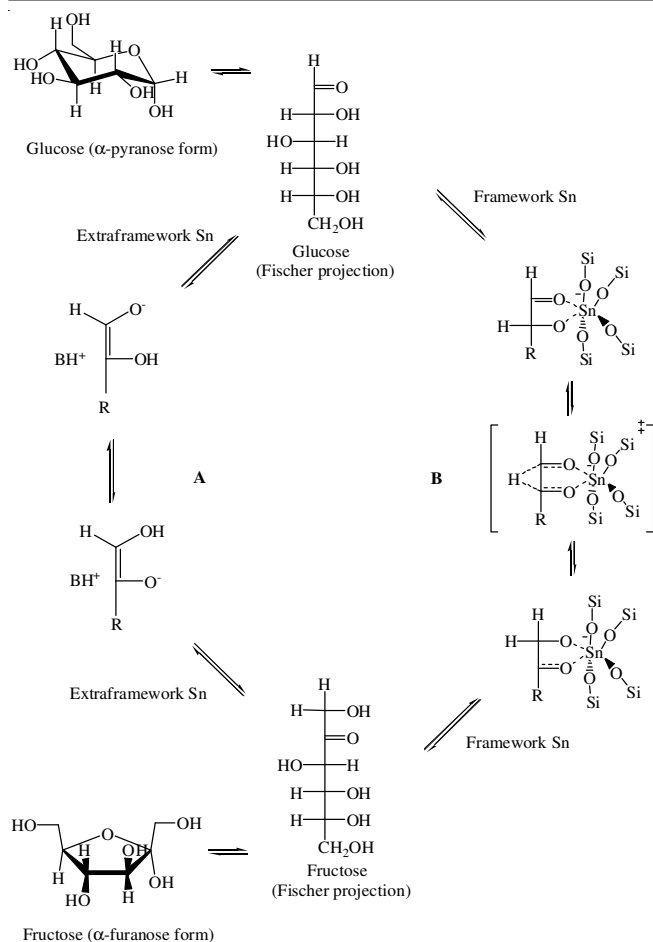


Fig. 3. Schematic representation of glucose isomerization mechanism using Sn- β zeolites in water by way of A) proton transfer and B) intramolecular hydride shift

The synthesis time of Sn- β zeolite is up to 40 days and the corrosive hydrogen fluoride is indispensable. Therefore, a one-step synthesis of active Sn-silicate catalysts by plasma enhanced chemical vapor deposition (PECVD) technique could prove to be a more straightforward method for the synthesis of heterogeneous Lewis acid catalysts for the isomerization of glucose to fructose⁴⁹. Yield of fructose reached nearly 17 %, which was in the same order as most of the Sn-containing catalysts that were reported by Moliner *et al.*²⁶. PECVD technique avoids the use of environmentally harmful solvents and it is a one-step synthesis procedure, improving the labor efficiency⁵⁰.

Isomerization of glucose by aluminates: The use of aluminate, such as an alkali or alkaline earth aluminate, for the isomerization of glucose to fructose in aqueous solution was reported in some patents claiming yields of 70-85 % of fructose, but the catalyst needed to be neutralized by acid prior to be removed by filtration⁵¹⁻⁵⁴. The optimal reaction conditions were as follows: 100 g glucose and 58 g potassium aluminate were dissolved in 100 mL water and the temperature was maintained at 328 K for 3 h⁵⁴. The mechanism for the isomerization of glucose to fructose by sodium aluminate in aqueous solution was involving transformation of a β -D-glucopyranose-1,3-aluminate complex into an α -D-fructofuranose-1,3,6-aluminate complex through an enol-aluminate complex, as illustrated in Fig. 4⁵⁵.

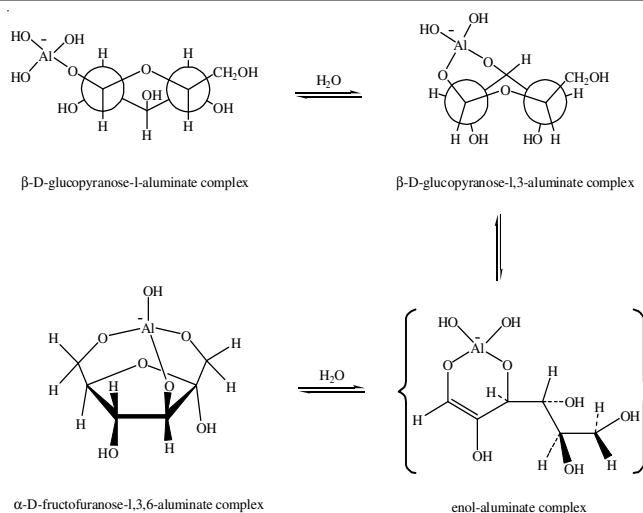


Fig. 4. Theorized mechanism for the isomerization of glucose to fructose by sodium aluminate

Sodium aluminate was also used as a heterogeneous catalyst in organic solvent mixtures for the isomerization process of glucose to fructose to lead up to 72 % selectivity of fructose for 68 % conversion of glucose. Isomerization was carried out at 328 K for 3 h. This process used glucose at 70 % dry matter, the mass ratio of sodium aluminate and glucose was 32 % and the solvent mixtures was composed of water, propylene glycol (PG) and dimethylsulfoxide (DMSO) with the mass ratio of 3/5/2. The catalyst was recycled four times with little decrease of the selectivity⁵⁶. The resulting carbohydrates solution could be directly dehydrated without any purification to afford HMF.

Isomerization of glucose in hot-compressed water (HCW): Hydrothermal conversion using hot compressed water (HCW) is an attractive approach for processing of sugars and lignocellulosic feedstock due to its advantages on environmental friendliness and potential on reaction control through use of water density⁵⁷⁻⁶¹. Chemical reactions in hot compressed water can be enhanced by water which can act as solvent, reactant and catalyst in the systems⁶².

Isomerization between glucose and fructose proceeded in subcritical water at the temperature as low as 403 K at a constant pressure of 5 MPa at a low initial glucose concentration (0.8 %). The reaction was accelerated by Pt nanoparticles protected by polyethyleneimine (Pt-PEI) and H₂. The rate of isomerization of glucose to fructose in the presence of Pt-PEI and H₂ was approximately three times greater than the rate of the reverse reaction. Yield of fructose was 19 % under the reaction condition, which was that the mixture of 1 g Pt-PEI and 60 mL 0.8 % glucose solution was stirred at 1100 rpm at 403 K for 3 h under a hydrogen atmosphere of 5 MPa. Pt-PEI were contained 0.5 wt. % Pt and 1 wt. % polyethyleneimine⁶³. These results are potentially significant for the future improvement of yield and selectivity in biomass conversions. Moreover, the reaction mechanism needs for further research.

Conclusion and outlook: So far, much work has been done on chemical isomerization of glucose to fructose as well as mechanisms of the isomerization reaction by using varied chemical catalysts. Efficient chemical catalysts maintain high activity over multiple cycles and work over a wide range of

temperatures so as to reduce product cost, compared with biological enzyme catalyst. Therefore, chemical isomerization of glucose to fructose may be possible to substitute the immobilized biocatalytic process for fructose production in the near future. Indeed, further studies should be carried out not only to acquire efficient chemical catalysts, but also to find a feasible industrialized production process.

The chemical isomerization of glucose to fructose is a complex production process, which is affected by several technological conditions. Specially, the formation of by-products can be minimized by appropriate design of the isomerization process, type of catalyst used and glucose quality. In addition, designing a practicable industrial process of glucose isomerization to fructose using chemical catalyst requires a comprehensive consideration of pre-isomerization, isomerization and post-isomerization processes. Chemical isomerization of glucose to fructose must be preceded by fructose yields with expected quality and optimal glucose/catalyst ratio. Moreover, the product quality can be controlled during separation of fructose from the reaction solution by application of appropriate post-processing parameters. In conclusion, the overall knowledge of pros and cons of the chemical isomerization process is needed in order to design optimal technological process for fructose industrialized production with a minimum of by-products and to obtain the final product of desired quality for various applications.

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