RECENT TRENDS IN CONVERSION OF C_6-SUGARS INTO VALUE-ADDED CHEMICALS OVER SOLID CATALYSTS

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In recent decades, the energy demand is ever increasing. Biomass energy is a viable option as an alternative due to reduced CO_2 emissions and depletion of fossil fuels at a faster rate. Therefore, the substitution of non-renewable fossil resources by renewable biomass as a sustainable feedstock has been focused on researchers to develop useful green fuels and other platform chemicals such as biofuels, commodity chemicals, and new bio-based materials. For the conversion of sugars, several methodologies have been investigated through chemocatalysis from plant-derived biomass feedstocks. This review critically overviewed the latest advancement regarding reaction conditions, product yields, and selectivity on the conversion of C_6-sugars into important chemicals like 5- hydroxymethylfurfural, levulinic acid, lactic acid, formic acid, glyceraldehyde, 1,3-dihydroxyacetone and furan-2,5-dicarboxylic acid, etc. This review describes green chemistry principles includes the main reactions used to convert renewable biomass into industrially important products that are applicable as raw materials with emphasis on preparative organic synthesis.

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INTRODUCTION

For the past few decades, the world is facing a lack of fossil fuel resources, which play an important role in our daily life by providing fuel, electricity and heating sources. Along with this, due to the increasing prices of petroleum oil and CO_2 emission, it is an urgent need to find some renewable energy sources like wind, solar and biomass.[1] Among these, biomass is the only renewable resource with fixed carbon, which is essential for the production of fuels and bio-based chemicals.[2] The annual production of carbohydrates is approximately 130 billion tons, due to which the biomass conversion into value-added products has a promising future.[3-5]

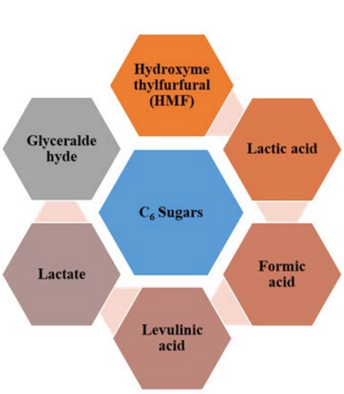

Figure 1. Main products of biomass conversion.

The major categories of biomass are shown in Scheme 1. Among these, lignocelluloses (cellulose, hemicellulose and lignin) are the most commonly available and utilized. The basic composition of lignocellulose is as follows: i) cellulose (40–60 %), ii) hemicellulose (20–40 %), lignin (10–24 %), and ashes (1–5 %).[6] Cellulose and hemicellulose further degrade into sugars, which then convert into different value-added products. Ever since sugars are a rich and renewable feedstock, so in this review, we have covered only glucose and fructose as feedstock to convert them into value-added products. Different value-added products that can form by glucose and fructose are summarized in Scheme 1.

Several studies have been done on the use of homogeneous and heterogeneous catalysts for the conversion of sugars into value-added products. For the production of these chemicals, several homogeneous catalysts such as Lewis acids, organic acids, inorganic acids, salts, and others are widely used. However, these homogeneous catalysts are easily soluble in the reaction medium and thus enhance the rate of the reaction with high selectivity of the desired product. Despite this, these catalysts have some drawbacks as it is very difficult to separate them from the reaction mixture as well as they can't be recycled for long term use. In this context, the synthesis of recyclable and easily separable solid catalysts has received much attention for the conversion of sugar into value-added chemicals. In this regard, several solid catalysts like porous zeolites, metal oxides, SO_3H- carbon/silica, and supported metal catalysts are reported to show high catalytic activity towards the high conversion of sugar into value-added products.[7-10] Along with this, different Brønsted and Lewis acid catalysts such as metal-substituted zeolites, surface-modified metal oxides, and cation-exchange resins are also well reported to convert sugar into some industrially important chemicals like polyols, furans, and acids.

This review mainly focuses on the potential applications of several solid acid catalysts for the conversion of C_6-sugars into value-added chemicals.

CONVERSION OF C6-SUGARS INTO VALUE-ADDED PRODUCTS OVER SOLID CATALYSTS

Synthesis of 5-hydroxymethyl-2-furaldehyde (HMF)

HMF is a vital platform chemical that can be further used to produce some important chemicals like polymer resins, solvents, and chemical intermediates.[11-13] It can also be converted into gasoline or diesel range fuels (C_9–C_{15}).[14] The synthesis of HMF can be done using acid-catalyzed dehydration of biomass. Several solid catalysts are reported to convert sugar into HMF, such as α-L-ZrP_2O_7, Lγ-ZrP, ZrO_2, TiO_2 and sulfonated carbon, etc.[15-16] Thus formed HMF can further convert into levulinic acid (LA) in the presence of acids.[17-19] The different solid catalysts used for the conversion of sugars into HMF are summarized in Table 1.

Table 1. Conversion of C_6-sugars into HMF Synthesis of levulinic acid (LA) (F=Fructose, G= glucose)

Catalyst	Sugar	Reaction conditions	Yield, %
H- Mordenite	F	165 °C/30 min	35[20]
Steamed BEA	G	180 °C/180 min	43[21]
Sn-BEA/Amber-lyst-70	G	130 °C/30 min	63[22]
TiO_2	G	200 °C/5 min	18.6[23]
ZrO_2	G	200 °C/5 min	10[23]
Nb_2O_5	G	120 °C/180 min	12[24]
Amberlyst-15-HT	G	100 °C/180 min	42[25]
Titanium nanotubes	G	120 °C/180 min	14[26]
Ta_2O_5	G	160 °C/140 min	58[27]
Nb/CB-2-DP	G	170 °C/120 min	20[28]
$AlEt_3$	G	140 °C/6 h	51[29]
Cr-NP	G	140 °C/6 h	49[30]
γ- TiP	F	100 °C/30 min	35.3[31]
C- ZrP_2O_7	F	100 °C/30 min	44.3[31]
rGO-SO_3H	G	180 °C/3 h	21.21[32]
TiO_2	G	160 °C/6 h	30[33]

An other important platform chemical is Levulinic acid (LA), which can be further converted into some other chemicals like liquid fuels, spice, cosmetic, pharmaceutical, pesticide, and fungicide.[34] The production of levulinic acid is a two-step process. In the first step, sugar is converted into HMF, which further convert into LA by rehydration process in the presence of solid acids. Catalytic dehydration of C_6-sugars to LA over strong cation exchange resin is well reported in the literature. The results indicated that with fructose, the yield of LA was 74.6 % at 110 °C and with glucose, it was 70.7 % of yield at 145 °C.[35] The different solid acid catalysts used for the conversion of sugar into LA are summarized in Table 2.

Table 2. Conversion of C_6 sugars into LA (F=Fructose, G= glucose)

Catalyst	Sugar	Reaction conditions	Yield, %
Fe/HY Zeolite	G	180 °C/180 min	60[36]
Ly_2HPW	G	130 °C/30 min	47.9[37]
Anhydrous $C_2H_2O_4$ with $Al(CF_3SO_3)_3$	G and F	180 °C/5 h	39.9[38]
$Al_2(SO_4)_3$	G	473 K/6 h	14.53[39]
Nafion NR50	F	120 °C/24 h	41[40]
Sulfonated graphene oxide	G	200 °C/2 h	50[41]
CP-SO_3H-1.69	G	170 °C/10 h	28.5[42]
Al- Zr oxide	G	180 °C/2 h	3.9[43]
Zirconium Phosphate	G	160 °C/3 h	14[44]
Amberlyst-70	G	160 °C/3 h	21.7[44]
$CrCl_3$ + HY Zeolite hybrid catalyst	G	160 °C/3 h	40[45]

Synthesis of formic acid (FA)

Formic acid is an important monocarboxylic acid and one of the glucose decomposition products. Due to which it counts as an interesting candidate for cellulose hydrolysis.

FA's broad applications include its use as a feed additive, for leather tanning, asdrilling fluid, as an acidifier, as a cleaning agent, or as an anti-icing substance for roads and airport runways.

Along with this, it has also been used as a hydrogen source in direct formic acid fuel cells (DFAFC). Due to the high efficacy and safety of DFAFC, it is also considered as an alternative to methanol and hydrogen fuel cells. Therefore the conversion of Sugars into FA is of great importance. Some commonly used solid catalysts are given in Table 3, which are used to convert C_6-sugars into FA.

Table 3. Conversion of C_6 sugars into Formic acid (F=Fructose, G= glucose)

Catalyst	Sugar	Reaction conditions	Yield, %
rGO-SO_3H	G	200 °C/3 h	14.18[32]
rGO-SO_3H	G	200 °C/4 h	10.30[32]
rGO-SO_3H	G	180 °C/3 h	13.05[32]
SAPO-5	G	100 °C/3 h	-[46]
CoAPO-5	G	100 °C/6 h	-[46]
SnAPO-5	G	100 °C/6 h	-[46]
HPA-5	G	90 °C/24 h	99[47]
LiOH	G	Room temp./8 h	91.3[48]

Synthesis of lactic acid

Lactic acid is an important renewable feedstock used for the preservation, coloring, and flavoring of food. Also, it can be used in the textile and pharmaceutical industries.[49] The synthesis of poly lactic acid (PLA) from lactic acid is also reported in the literature. Lactic acid show two enantiomeric forms, l-(+) and d-(−), which affect the physicochemical properties of the polylactide polymer.[50]

The conversion of glucose and fructose into racemic methyl lactate have been performed over Lewis acidic zeolites and zeotypes catalysts under optimized reaction conditions.[51]Table 4 summarizes the conversion of C_6-sugars into lactic acid and lactate over different solid catalysts.

Table 4. Conversion of C_6 sugars into other Lactic acid and lactate.

Catalyst	Sugar	Reaction onditions	Product/yield in %
rGO-SO_3H	G	180°C/3 h	Lactic acid/5.51[32]
Sn-C-MCM-41	G	160°C/20 h	Lactate/17[36]
Sn- MWW	G	160°C/20 h	Lactate/44[37]
Sn- BEA	G	160°C/20 h	Lactate/43[52]
Sn- BEA	F	160°C/20 h	Lactate/44[53]

CONCLUSIONS AND FUTURE OPPORTUNITIES

In the recent scenario, renewable biomass plays an important role in the production of several value-added products such as biofuels, bioplastics and other fine chemicals. For conversion of this renewable biomass, particularly sugars, various solid catalysts like supported metal catalysts, micro and mesoporous materials, metal oxides, and sulfonated polymers are found efficient and environmentally friendly. Several Bronsted and Lewis acid catalysts for converting C6-sugars into value-added chemicals such as HMF, LA, FA and lactic acid are well reported in the literature. Though almost all the solid catalyst can be easily separated from the reaction mixture after completion of the reaction and reused in the next reaction cycle, efforts should be made for complete recovery of the catalysts without any loss in their catalytic efficiency. Along with this, under some reaction conditions, leaching of ions from the solid catalysts undergoes, which decreases the efficiency of the catalysts.

To overcome this problem, some novel catalytic materials of high stability should be designed, which will increase the percentage conversion of biomass into value-added products.

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