Steven L. Suib

Editor

New and Future Developments in Catalysis
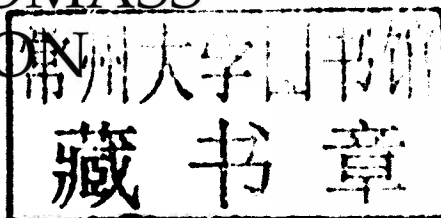
Catalytic Biomass Conversion

NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

CATALYTIC BIOMASS CONVERSION

Edited by

STEVEN L. SUIB

*Department of Chemistry and Chemical Engineering
and Institute of Materials Science, The University of Connecticut,
Storrs, CT 06269-3060*

For information on all Elsevier publications
visit our web site at store.elsevier.com

Working together
to grow libraries in
developing countries

www.elsevier.com • www.bookaid.org

NEW AND FUTURE DEVELOPMENTS IN CATALYSIS

Contributors

Marco A. Báez-Vásquez Jupiter Biotechnologies, LLC, Jupiter, FL, USA

Damian K. Barnard School of Engineering, University of Edinburgh, UK

Subhash Bhatia School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300 NibongTebal, Penang, Malaysia

Fred V. Carstensen Connecticut Center for Economic Analysis, University of Connecticut, School of Business, 2100 Hillside Road, Storrs, CT 06269-4087, USA

School of Business, University of Connecticut, CT, USA

G. Dautzenberg Research Institute Bioactive Polymer Systems e.V. and Brandenburg University of Technology Cottbus, Kantstrasse 55, D-14513 Teltow, Germany

Stephen L. Dellaporta Yale University, Department of Molecular Cellular and Developmental Biology, New Haven, CT 06520-8104, USA

Arnold L. Demain The Charles A. Dana Research Institute for Scientists Emeriti (R.I.S.E.), HS-330, Drew University, Madison, NJ 07940, USA

Adam Deresienski University of Rhode Island, Department of Cell and Molecular Biology, West Kingston, RI 02892, USA

Philip W. Dyer Centre for Sustainable Chemical Processes, Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Kresten Egeblad Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

Alistair Elfick School of Engineering, University of Edinburgh, UK

SynthSys Synthetic and Systems Biology, University of Edinburgh, UK

Eugene Fletcher School of Biological Sciences, University of Edinburgh, UK

Christopher E. French School of Biological Sciences, University of Edinburgh, UK

SynthSys Synthetic and Systems Biology, University of Edinburgh, UK

Atsushi Fukuoka Catalysis Research Center, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

Pierre Gallezot Institut de recherches sur la catalyse et l'environnement, Université de Lyon/CNRS, 2 avenue Albert Einstein, 69626, Villeurbanne Cedex, France

Aharon Gedanken Department of Chemistry and Kanbar Laboratory for Nanomaterials at the Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel

M. Gerhardt Research Institute Bioactive Polymer Systems e.V. and Brandenburg University of Technology Cottbus, Kantstrasse 55, D-14513 Teltow, Germany

Marcello Graziano Connecticut Center for Economic Analysis, University of Connecticut, School of Business, 2100 Hillside Road, Storrs, CT 06269-4087, USA

H. Christopher Greenwell Centre for Sustainable Chemical Processes, Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Department of Earth Sciences, Durham University, South Road, Durham, DH1 3LE, UK

Joel Hague University of Rhode Island, Department of Cell and Molecular Biology, West Kingston, RI 02892, USA

Siti Salwa Hashim School of Chemical Engineering, Universiti Sains Malaysia, Seri Ampangan, 14300 NibongTebal, Penang, Malaysia

Lei Jin Central R&D, MacDermid Electronic Solutions, MacDermid Inc., 227 Freight St. Waterbury, CT 06702, USA

B. Kamm Research Institute Bioactive Polymer Systems e.V. and Brandenburg University of Technology Cottbus, Kantstrasse 55, D-14513 Teltow, Germany

Steven D. Kane School of Biological Sciences, University of Edinburgh, UK

Albert P. Kausch University of Rhode Island, Department of Cell and Molecular Biology, West Kingston, RI 02892, USA

Hirokazu Kobayashi Catalysis Research Center, Hokkaido University, Kita 21 Nishi 10, Kita-ku, Sapporo, Hokkaido 001-0021, Japan

Miri Koberg Department of Chemistry and Kanbar Laboratory for Nanomaterials at the Bar-Ilan University Center for Advanced Materials and Nanotechnology, Bar-Ilan University, Ramat-Gan 52900, Israel

Chung-hao Kuo Department of Chemistry, University of Connecticut, USA

Sahreena Saleem Lakhundi School of Biological Sciences, University of Edinburgh, UK

Li Li Centre for Sustainable Chemical Processes, Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Yi Li University of Connecticut, Department of Plant Science and Plant Science and Landscape Architecture, Storrs, CT 06269, USA

Chao-Kuo Liu School of Biological Sciences, University of Edinburgh, UK

Kimberly Nelson University of Rhode Island, Department of Cell and Molecular Biology, West Kingston, RI 02892, USA

Iman Noshadi University of Connecticut, Institute of Materials Science and Chemical Engineering Program, CT, USA

Christian Mårup Osmundsen Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

Department of Physics, Technical University of Denmark, Anker Engelundsvej 1, DK-2800 Lyngby, Denmark

Richard S. Parnas University of Connecticut, Institute of Materials Science and Chemical Engineering Program, CT, USA

Kathryn E. Parr Connecticut Center for Economic Analysis, University of Connecticut, School of Business, 2100 Hillside Road, Storrs, CT 06269-4087, USA

Michael Pomykala University of Connecticut, Institute of Materials Science and Chemical Engineering Program, CT, USA

Jack S. Rowbotham Centre for Sustainable Chemical Processes, Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Department of Chemistry, Durham University, South Road, Durham, DH1 3LE, UK

Bobban Subhadra MIOX Corporation and GreeInn Solutions LLC, Albuquerque, NM 87113, USA

Steven L. Suib Department of Chemistry, University of Connecticut, USA

Institute of Materials Science, University of Connecticut, USA

Chemical, Materials & Biomolecular Engineering, University of Connecticut, U-3060, 55 North Eagleville Rd., Storrs, CT 06269-3060, USA

Esben Taarning Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark

Michael Tilelli University of Rhode Island, Department of Cell and Molecular Biology, West Kingston, RI 02892, USA

Natalia Vorotytseva Department of Geography, University of Connecticut, 215 Glenbrook Road, Storrs, CT 06269-1063, USA

William E. Waite Connecticut Center for Economic Analysis, University of Connecticut, School of Business, 2100 Hillside Road, Storrs, CT 06269-4087, USA

Z. Conrad Zhang Dalian National Laboratory for Clean Energy, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, 116023, China

Contents

7. Hybrid Plant Systems for Breeding and Gene Confinement in Bioenergy Crops

ALBERT P. KAUSCH, ADAM DERESIENSKI, JOEL HAGUE, MICHAEL TILELLI, STEPHEN L. DELLAPORTA, KIMBERLY NELSON, AND YI LI

8. An Introduction to Pyrolysis and Catalytic Pyrolysis: Versatile Techniques for Biomass Conversion

LI LI, JACK S. ROWBOTHAM, H. CHRISTOPHER GREENWELL, AND PHILIP W. DYER

9. Using Microwave Radiation and SrO as a Catalyst for the Complete Conversion of Oils, Cooked Oils, and Microalgae to Biodiesel

MIRI KOBERG AND AHARON GEDANKEN

10. Environmental Benefits of Integrated Algal Biorefineries for Large-Scale Biomass Conversion

BOBBAN SUBHADRA

11. Heterogeneous Catalysts for Biomass Conversion

LEI JIN, CHUNG-HAO KUO, AND STEVEN L. SUIB

1

Metal Catalysts for the Conversion of Biomass to Chemicals

Pierre Gallezot

Institut de recherches sur la catalyse et l'environnement,
Université de Lyon/CNRS,
2 avenue Albert Einstein, 69626,
Villeurbanne Cedex, France

1.1 INTRODUCTION

Extensive literature surveys on biomass conversion to chemicals were recently published [1–9] revealing the rapid development of new catalytic systems and reaction media adapted to the structure of biomolecules. The present chapter deals with the design and performance of metal catalysts employed for the conversion of platform molecules obtained from carbohydrates, triglycerides, and terpenes into chemicals that are either already synthesized from fossil resources or consisting of new bioproducts with no synthetic counterpart. Bifunctional metal catalysts converting biopolymers such as starch, cellulose, and hemicellulose into a mixture of chemicals that could be employed for the manufacture of high tonnage end-products such as paper additives, paints, resins, foams, surfactants, lubricants, and plasticizers will also be considered [7,10]. Because the literature on catalytic biomass conversion is presently bursting and because a complete survey of catalytic systems was not possible in the framework of this chapter, focus will be laid on selected examples of biomass conversion catalyzed by metals, particularly hydrogenation, hydrogenolysis, and oxidation reactions.

1.2 HYDROGENATION CATALYSTS

1.2.1 Catalysts for the Hydrogenation of Carbohydrates and Derivatives

1.2.1.1 Hydrogenation of Glucose

More than 800,000 ton/y of sorbitol are produced industrially by catalytic hydrogenation of D-glucose, a cheap and abundant feedstock obtained from starch-containing crops such as maize, wheat, and potatoes. Sorbitol is used as additives in many industrial products, particularly in the food, cosmetic, and paper industries, and as building block for the synthesis of various fine chemicals including vitamin C (Figure 1.1). Highly active and stable metal catalysts are required for the industrial hydrogenation of glucose. Because selectivities higher than 99.5% to sorbitol at total glucose conversion are required for a number of applications epimerization of sorbitol to mannitol and Cannizarro reaction to gluconic acid should be avoided. The requirements for a long-term stability toward metal leaching and sintering were well documented, but the leaching of supporting materials in highly chelating reaction media was often overlooked in the literature. Also, the deactivation of metal catalysts by impurities in glucose feedstock, or formed by side reactions, and the procedures of catalyst regeneration were seldom studied. Although sorbitol is a high tonnage commodity product, hydrogenation reactions are still mainly carried out discontinuously in stirred tank reactors at 373–453 K and 5–15 MPa of H_2 pressure in the presence of suspended catalyst powders. The design of catalyst formulation to replace the prevailing batchwise production by continuous processes is not well documented.

Most of the current industrial production of sorbitol is performed in stirred tank reactors loaded with Raney-type nickel catalysts (sponge nickel, skeletal nickel) promoted by various transition metals. Nickel catalysts present the advantage of a relatively low price and because of their high density they are easily separated from the liquid phase by sedimentation possibly accelerated by magnetic methods. Raney-type nickel catalysts are often prepared from Ni–Al–M alloys where M stands for transition metals such as Mo, W, or Cr, added to nickel-aluminum melt at a concentration of 0.5–5 mol%. The alloy is then attacked with alkali solutions to remove part of the aluminum and yield highly porous, tri- or polymetallic catalysts. Alternatively, metal promoters could be added to skeletal nickel by various methods of surface deposition. The presence of metal promoters favors the stability of the porous framework and accelerates reaction rates [11–13]. Glucose hydrogenation was studied in a well-stirred, high pressure batch reactor on Mo-, Cr-, and Fe-promoted Raney-type nickel catalysts prepared by soda attack on Ni–Al–M alloys [12]. Sn-promoted catalysts were obtained by controlled surface
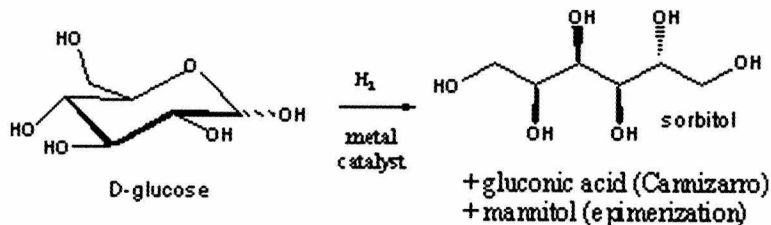

FIGURE 1.1   Glucose hydrogenation to sorbitol.

reaction of $Sn(Bu)_4$ on the hydrogen-covered surface of a Raney Nickel obtained from a Ni_2Al_3 alloy. The promoted catalysts were up to seven times more active provided that metal promoters were homogeneously distributed with an optimum concentration. The rate enhancement was attributed to the polarization of C=O bonds of the aldehyde form of glucose by electropositive metal promoters acting as Lewis acid sites. Iron- and tin-promoted catalysts deactivated very rapidly because the promoters were leached away from the surface. In contrast, the aging of molybdenum and chromium-promoted catalysts was attributed to the poisoning of the active sites by organic species. The major cause of deactivation of commercial Raney-type nickel catalysts was the presence of gluconic acid formed by the Cannizarro reaction poisoning catalytic sites and favoring nickel leaching [14], but after many recycles under industrial operation the loss of active surface area due to metal sintering was also a cause of deactivation [12]. Several attempts have been made to use supported nickel catalysts as substitutes for Raney-type nickel. Because of the high nickel loadings required (typically >40 wt.%) to obtain a sufficient activity in industrial operating conditions, the specific surface area of nickel was usually quite low. The kinetics of hydrogenation of 40 wt.% glucose solution was studied in a trickle-bed reactor in the presence of an industrial catalyst based on extrudates of kieselguhr-supported nickel catalysts containing 48.4 wt.% nickel [15]; the catalyst activity was low (5 mmol h^{-1} g_{Ni}^{-1} at 403 K, 8 MPa) and decreased with time because of the progressive leaching of nickel and support in the reaction medium. $Ni-B/SiO_2$ amorphous catalyst prepared by reduction with KBH_4 aqueous solutions exhibited a higher activity (TOF: $0.024 s^{-1}$) than commercial Raney-type catalysts (TOF: $0.013 s^{-1}$) [16]. Ni/SiO_2 catalysts prepared by various methods deactivated by metal leaching, metal sintering, and support degradation [17]. Ni/SiO_2 catalysts prepared by impregnation with nickel ethylenediamine complexes did not leach significantly after 5 h on stream, but they were slightly less active than commercial catalysts and less selective to sorbitol [18].

Because nickel catalysts are prone to leaching and sintering and because their activities are comparatively low, the present trend is to develop industrial processes based on supported ruthenium catalysts. Comparison of the specific activities measured on nickel and ruthenium catalysts under the same reaction conditions showed that ruthenium was 20–50 times more active than nickel per mass of metal. Specific reaction rates measured over various ruthenium catalysts are given in Table 1.1. Rates measured in trickle-bed reactor were lower compared to stirred tank reactors because of mass transfer limitation between the solid, liquid, and gas phases. Carbons of various origins have been widely used as supporting material for ruthenium because of their resistance to leaching, and because they adsorb organic impurities present in feedstocks thus preventing to some extent the poisoning of ruthenium surfaces. The hydrogenation activities of Ru/C catalysts in slurry reactors were proportional to the ruthenium surface area and independent of the preparation method [13,19]. Activated carbon cloths (ACC) present significant advantages with respect to conventional activated carbons such as efficient mass transfer from the liquid phase, no necessity of decantation or filtration, and high flexibility to fit into any reactor geometry [20,21]. ACC were prepared from woven rayon cloths carbonized at 1200 °C under nitrogen and activated at 900 °C under CO_2; 0.9 wt.% Ru/ACC catalysts were very active (2.40 mol h^{-1} g_{Ru}^{-1}) and selective to sorbitol (99.5% at 99.7% conversion) and could be easily recycled. The catalytic performances were even better with 10 wt.% Pt/ACC catalysts (Table 1.1). In most studies the selectivity to sorbitol was higher than 98% at total glucose conversion, but the selectivity decreased as the time of contact of

TABLE 1.1   Reaction Data on Glucose Hydrogenation Over Ruthenium Catalysts

Catalyst	Conditions	Activity (mol h^{-1} g$_{metal}^{-1}$)	Selectivity	Ref.
1.6% Ru/C	trickle-bed reactor 40 wt.% glucose, 100 °C; 8 MPa	0.7 (at 98.5% conversion)	99.6% at 98.5% conv.	[19]
5.6% Ru/C	10 wt.% glucose, 120 °C, 4 MPa		>98%	[14]
0.9% Ru/ACC	40 wt.% glucose, 100 °C; 8 MPa	2.4	99.5% at 99.7% conv.	[20]
10% Pt/ACC	40 wt.% glucose, 100 °C; 4 MPa	1.8	99.5% at 100% conv.	[20,21]
5% Ru/C nanotubes	40 wt.% glucose, 100 °C, 4 MPa	TOF 168 h^{-1} at 62% conv.		[24]
Amorphous Ru$_{89}$–B$_{11}$	50 wt.% glucose, 80 °C, 4 MPa	0.5		[25]
4.5% Ru/SiO$_2$	50 wt.% glucose, 100 °C, 8 MPa	6.0		[26]
0.27% Ru/TiO$_2$	40 wt.% glucose, 100 °C, 12 MPa	11.5		[17]

catalyst with sorbitol solution increased because sorbitol was subject to further conversion to mannitol. Thus, the selectivity decreased as the time of contact with a Ru/C catalyst loaded in a trickle-bed reactor was increased beyond 100% conversion [19]; however, using a Pt–Ru/C bimetallic catalyst containing 1.6 wt.% of ruthenium and 0.2 wt.% of platinum it was possible to maintain a selectivity higher than 99% even after a long contact time. After long time on stream in the trickle-bed reactor, a Ru/Al$_2$O$_3$ catalyst deactivated because of structural modification of alumina and of ruthenium poisoning by sulfur compounds, gluconic acid, and deposition of iron atoms leaching from the reactor walls [22]. The loss of conversion from 99.9% to 98% experienced by a Ru/Al$_2$O$_3$ catalyst after 1080 h on stream was also attributed to the poisoning of ruthenium by metallic species leached out from the reactor walls [17]. A 3.7% loss of activity was experienced by a 1.6% Ru/C catalyst after 596 h on stream in a trickle-bed reactor, but the selectivity to sorbitol remained stable at 99.3% and no leaching or sintering of ruthenium was detected [19]. However, glucose solutions employed industrially are liable to contain more impurities than those used in academic investigations leading to a faster deactivation because of the deposition of organic species on the catalyst surfaces. Thus, an industrial 5% Ru/C catalyst lost 25% of its activity after 300 h on stream as a low purity grade glucose solution was hydrogenated in a trickle-bed reactor [23]; a partial recovery of catalyst activity was obtained by oxidation with diluted hydrogen peroxide solutions of the organic species deposited on the catalyst surface.

1.2.1.2 Hydrogenation of Fructose

The hydrogenation of fructose leads to sorbitol and mannitol which has a high added value as low caloric sweetener (Figure 1.2). The challenge was to maximize by an appropriate choice of metal catalysts and reaction conditions the yield to mannitol. Sorbitol and mannitol are formed by hydrogenation of two different cyclic forms of fructose and copper catalysts favor the formation of mannitol [27]; the selectivity ratio (mannitol formed/fructose converted) was 0.8 on Cu/SiO$_2$ catalysts while this ratio was close to 0.5 for other supported metal catalysts. The kinetics of fructose hydrogenation over a copper catalyst (61 wt.% CuO and 39 wt.% ZnO) in aqueous solutions were studied in a batch reactor operating at 35–65 bar and between 90 and
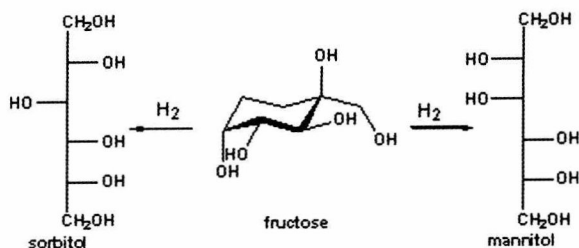
FIGURE 1.2 Hydrogenation of fructose.

130°C [28]; the mannitol selectivity was within 60–68% and improved slightly as the hydrogen pressure increased or the reaction temperature decreased. The sonification during fructose hydrogenation reaction enhanced the reaction rate over Cu/SiO_2 and retarded catalyst deactivation, but had no influence on selectivity to mannitol [29]. Fructose hydrogenation was carried out over various Raney-type nickel and copper catalysts [30]; copper was less active than nickel, but favored the production of mannitol over sorbitol by a 2:1 ratio. Because copper catalysts have a low hydrogenation activity, attempts have been made to use more active ruthenium or platinum catalysts modified by metal promoters favoring mannitol selectivity. Thus, the selectivity to mannitol increased from 47% to 63% on Pt/C catalysts promoted by deposition of 1 wt.% tin on a commercial 5 wt.% Pt/C catalyst, but the catalyst activity decreased [31].

1.2.1.3 Hydrogenation of Xylose and Furfural

The acid-catalyzed hydrolysis of xylan-type hemicelluloses present in soft woods and straw yields C_5 sugars such as xylose, which can be further dehydrated to furfural (Figure 1.3). The hydrogenation of xylose into xylitol, a polyol widely employed as food, cosmetic, and pharmaceutical additives, is achieved industrially in the presence of promoted Raney-type nickel catalysts affording up to 98% yield, but catalysts deactivate by promoter leaching and surface poisoning. A slow deactivation was observed as catalysts were submitted to continuous ultrasound irradiation [32]. Ru/C catalysts exhibited a higher activity than Raney nickel and were less prone to deactivation. Thus 40 wt.% aqueous solutions of xylose were hydrogenated in
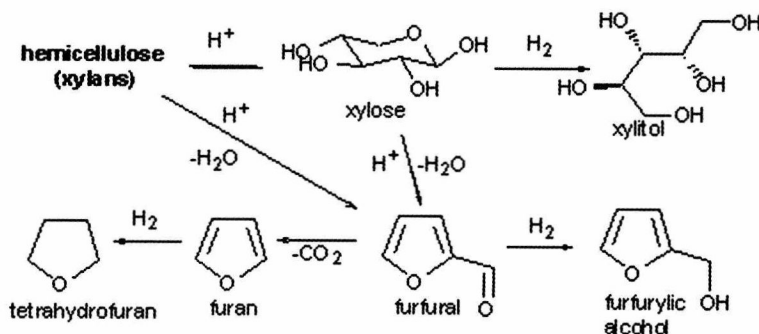

FIGURE 1.3 Hydrogenation of xylose and furfural.

a continuous reactor packed with Ru/SiO_2 and Ru/ZrO_2 catalysts affording a 99.9% yield to xylitol [33].

Furfural produced industrially by combined hydrolysis and dehydration of agricultural wastes or xylose on acid catalysts is hydrogenated industrially to furfuryl alcohol in the liquid or vapor phase over copper-chromite catalysts (Figure 1.3). A number of studies were aimed at finding more environmentally acceptable catalysts that could selectively hydrogenate the carbonyl group and preserve the $C{=}C$ bonds. The vapor phase hydrogenation at 473 K afforded a 98% yield over $Cu–Co/SiO_2$ [34] or over $Cu–MgO$ [35]. The liquid phase hydrogenation of furfural over supported $Pt–Sn_{0.3}$ catalyst prepared by controlled surface reactions of tin on Pt-catalyst yielded 98% of fufuryl alcohol [36]. A switchable system based on two consecutive fixed-bed flow reactors loaded with copper chromite and Pd/C catalysts, respectively, was designed to achieve the hydrogenation of furfural in supercritical CO_2 [37]; depending on temperature and H_2-concentration, furfural was hydrogenated selectively to furfuryl alcohol (97% yield), tetrahydrofurfuryl alcohol (96% yield), 2-methylfuran (90% yield), 2-methyltetrahydrofuran (82% yield), and furan (98% yield).

The vapor phase decarbonylation of furfural to furan was performed in a fixed-bed reactor at 260 °C on Pd/Al_2O_3 catalysts loaded with potassium carbonate to promote the decarbonylation and suppress hydrogenation side reactions [38]; for an optimum 8 wt.% potassium loading, a 99.5% yield to furan was obtained. A continuous hydrogenation of furan in supercritical CO_2 was achieved on 5 wt.% Pd-catalyst supported on aminopolysiloxane [39]; a 96% selectivity to THF at 98% conversion of furan was achieved while 1-butanol was the only side product formed by hydrogenolysis reactions. The hydrogenation of furan to THF was studied over Pt(1 1 1) and Pt(1 0 0) single-crystal surfaces and size-controlled 1.0, 3.5, and 7.0 nm Pt nanoparticles [40].

1.2.1.4 Hydrogenation of 5-Hydroxymethylfurfural

An extensive review of 5-hydroxymethylfurfural (HMF) production by dehydration of fructose and other carbohydrates and its use as a building block for chemical synthesis was published [4]. The main products obtained by catalytic hydrogenation of HMF over supported metal catalysts under various conditions are given in Figure 1.4. 2,5-dimethylfuran (2,5-DMF)
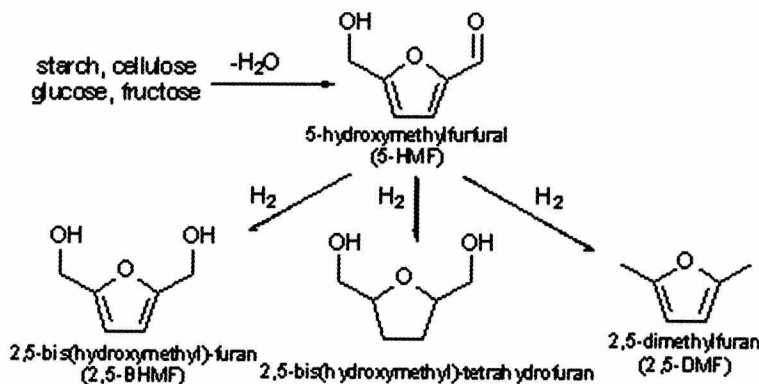

FIGURE 1.4   Hydrogenation of 5-hydroxymethylfurfural.

was obtained with a 71% yield by vapor phase hydrogenolysis of 10 wt.% HMF in 1-butanol solution in a flow reactor loaded with Cu–Ru/C catalyst [41]. A 95% yield to 2,5-DMF was obtained by heating a solution of HMF in refluxing tetrahydrofuran in the presence of formic acid, H_2SO_4, and Pd/C catalyst [42]. The hydrogenation of HMF dissolved in [EMIM]Cl and acetonitrile at 393 K under 62 bar of H_2 pressure over Pd/C resulted in a 32% selectivity to 2,5-DMF at 47% conversion [43]. 2,5-dimethyltetrahydrofuran was obtained with a 79% yield from fructose by hydrogenation in H_2O/toluene/HI mixture in the presence of $RhCl_3$ catalyst [44].

1.2.1.5 Hydrogenation of Levulinic Acid

Levulinic acid is obtained industrially with a 60% yield by combined acid-catalyzed hydrolysis and dehydration of cellulose and hemicellulose with the transient formation of HMF [45]. The hydrogenation to γ-valerolactone (GVL) (Figure 1.5) was extensively studied because of the unique physical and chemical properties of GVL which is an ideal liquid for use as a solvent, as an intermediate in the chemical industry, or for energy storage [46]. GVL was obtained with a 97% yield by hydrogenation of levulinic acid at 150 °C over a 5 wt.% Ru/C catalyst [47]. A continuous conversion over Ru/SiO$_2$ catalyst in supercritical CO$_2$ resulted in a 99% yield and allowed an easy separation of GVL from water [48]. Pt/TiO$_2$ or Pt/ZrO$_2$ catalysts afforded a 95% yield to GVL with marginal deactivation in a continuous reactor [49]. Vapor phase hydrogenation in a continuous fixed-bed reactor over 5 wt.% Ru/C catalysts afforded a 100% GVL yield for up to 240 h on stream without loss in activity [50]. The hydrogenation of levulinic acid to GVL was performed using formic acid as hydrogen donor in the presence of ruthenium-phosphorous complexes immobilized on SiO$_2$ [51]. The reduction of LA and its esters to GVL was also accomplished by catalytic transfer hydrogenation over various metal oxide catalysts using secondary alcohols as hydrogen donors [52]; ZrO$_2$ was highly active in both batch and continuous flow reactor studies affording up to 80% yield to GVL.

1.2.1.6 Hydrogenation of Succinic Acid

The bulk of succinic acid (SA) production is currently obtained from maleic anhydride produced by oxidation of n-butane or butadiene, but recent advances in fermentation from carbohydrates and purification technologies succeeded to make bio-based succinic acid economically attractive. The hydrogenation of succinic acid leads to 1,4-butanediol (BDO), γ-butyrolactone (GBL), and tetrahydrofuran (THF) that have a well-established market (Figure 1.6). The hydrogenation of succinic anhydride to GBL was achieved with a
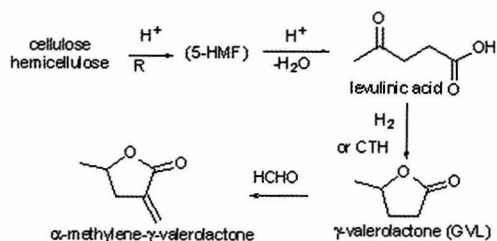

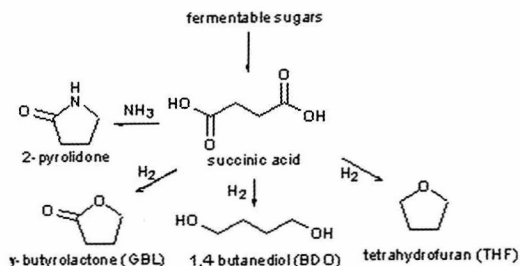FIGURE 1.5 Hydrogenation of levulinic acid.

FIGURE 1.6   Hydrogenation of succinic acid.

97% selectivity at 97% conversion on Au/TiO$_2$ catalysts promoted by small amounts of platinum favoring H$_2$ dissociation [53]. A 54% yield to GBL was obtained on Pd-catalysts supported on mesoporous aerogels and a correlation was established between the density of acidic sites and the final yield to GBL [54]. The selectivity to BDO, GBL, and THF was tuned by a proper choice of metal catalyst supported on Starbon® mesoporous carbon [55,56]; thus, Rh/Starbon® exhibited a 90% selectivity to BDO at 60% conversion while Ru/Starbon® was highly selective to THF.

Bio-sourced succinate obtained by fermentation is subjected to various purification technologies to eliminate proteins and organic acids present in fermentation broths, but remaining impurities are liable to poison the activity or modify the selectivity of catalysts. Thus the hydrogenation rate of bio-succinic acid over Pd–Re/C catalysts at 160°C under 150 bar of H$_2$-pressure was lower than on synthetic SA (100% conversion after 83 h vs. 46.5 h) and a lower selectivity to BDO (42% vs. 62%) was observed at 75% conversion [57]. A one-pot synthesis yielding 80% of 2-pyrrolidone was achieved by reacting succinic anhydride and ammonia in water solution at 250°C under 120 bar pressure over Au/TiO$_2$ catalysts [53].

1.2.1.7 Hydrogenation of Lactic Acid

Lactic acid (LA) produced by fermentation of carbohydrates was hydrogenated to 1,2-propanediol (PDO) over Cu/SiO$_2$ catalyst in vapor phase at 473 K affording a 88% yield [58] (Figure 1.7). A 65% selectivity at 95% LA conversion was achieved over Cu-catalysts prepared from copper hydroxysilicate catalysts [59]. The liquid phase hydrogenation of LA at 100–170°C and 7–14 MPa H$_2$-pressure over 5 wt.% Ru/C catalyst afforded an 86% yield to PDO [60]. The effect on the activity of Ru/C catalysts of residual fermentation impurities in LA has been studied [61]; whereas refined LA exhibited a stable conversion to PDO, and partially refined LA showed a steep decline in PDO production. The addition of model impurities to refined LA, such as organic acids, sugars, and inorganic salts, has little effect on conversion, while amino-acids (alanine, cysteine, methionine) resulted in irreversible catalyst deactivation (see Figure 1.7).

1.2.1.8 Hydrogenation of Arabinonic Acid

There is a great interest to convert C$_6$ carbohydrates available in large supply into C$_5$ or C$_4$ polyols which are valuable food or care product additives. Thus, glucose can be converted via a two-step process to arabitol. The first step is an oxidative decarboxylation of glucose into