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Springer

SpringerBriefs in Molecular Science

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Preface

Gold catalysts have been proven to possess a unique set of catalytic properties for a variety of reactions. The consequent interest in catalysis by gold has resulted in extensive research activity in this area. Biomass is a renewable and rich source of chemicals. New methods of biomass valorization involve catalytic transformations of biomass-derived compounds, and gold catalysts have been shown to be promising catalysts for the diverse reactions needed.

This book describes in brief the nature of the gold catalytic properties. The major part of the work covers various transformations of biomass-derived chemicals, including selective oxidation, hydrogenation, isomerization, acetalization, and amination reactions. The superior performance of gold catalysts discovered in the past 7 years is discussed in detail.

Contents

Chapter 1
Introduction

1.1 Introduction

Development of new technologies to supplement fossil resources led to a growing interest in the utilization of alternative processing routes. Biomass is a rich renewable feedstock for fine chemicals, polymers, and a variety of commodities that can potentially replace petroleum-derived chemicals. Carbohydrates, lignin, vegetable oils, and many other substances extracted from biomass are promising building blocks for valuable chemicals. Some of these important renewables are found in the waste of factories such as corn, pulp, and paper mills. Indeed, it was stated a decade ago that the use of biorenewable feedstocks will provide for the sustainable development of the chemical industry [1–3]. Already, a number of biorefineries are operating to convert biomass into diverse valuable chemicals.

Catalytic conversion of biomass, which reduces use of toxic chemicals, is one of the important approaches to improve profitability of biorefineries and biomass transformation opportunities have been reviewed some years ago [4–7]. Routes of catalytic transformations include basic chemical reactions such as selective oxidation, hydrogenation and isomerization, which can be performed using gold catalysts.

Utilization of gold catalysts for biomass conversion is a promising direction, since high-value chemicals can be produced in many of the reactions in which gold demonstrated outstanding activity and selectivity. Currently, there are many examples of successful application of gold in the catalytic conversion of biomass-derived compounds. In this review, we will focus on some of the gold-catalyzed transformations of renewable molecules into value-added chemicals reported in the last 7 years.

1.2 Biomass-Derived Compounds

Renewable feedstock derived from biomass is a rich source for chemical synthesis. Selected in this overview are biomass-derived compounds that are available for transformation over gold catalysts into value-added chemicals. An overview of the reaction pathways is summarized on Scheme 1.1.
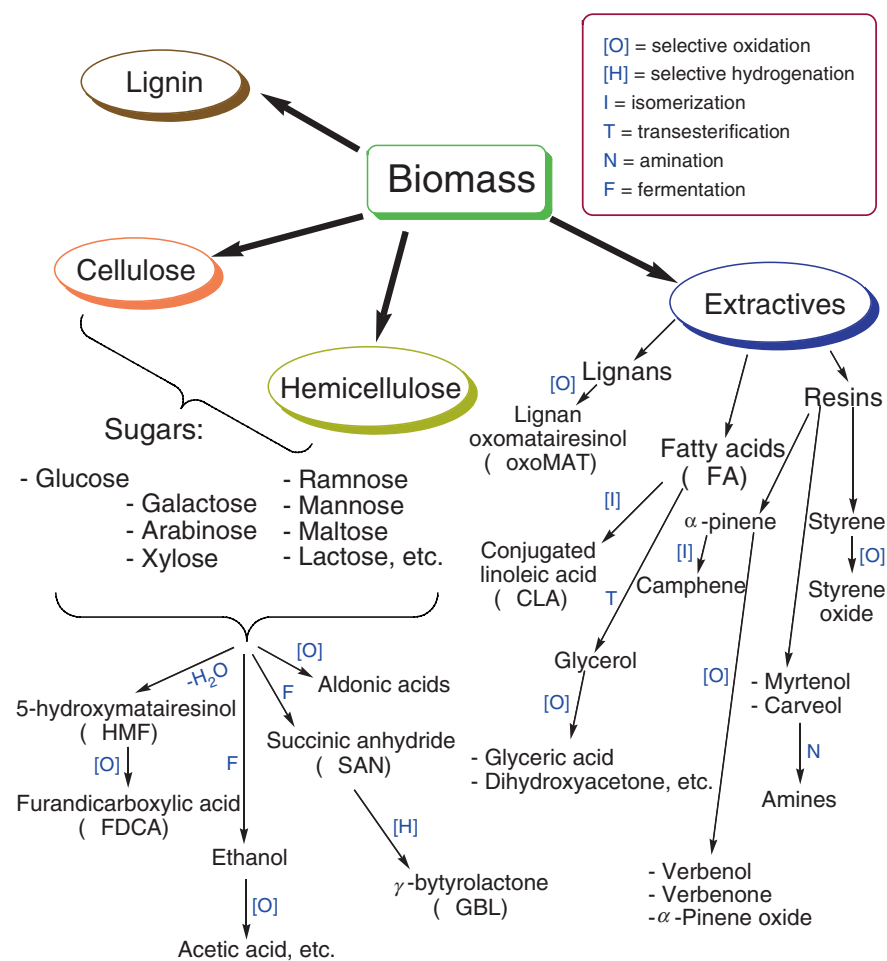
Scheme 1.1 Different catalytic routes for the biomass-derived compounds transformation over gold-based catalysts

1.2.1 Sugar-Derived Chemicals

The main components of woody biomass are cellulose (40–50 %), lignin (16–33 %), hemicelluloses (15–30 %), and extractives (1–10 %) [5]. Cellulose is a linear polymer containing up to 10,000 units of D-glucopyranose connected by glycosidic ether bonds. Hemicelluloses have a more heterogeneous structure than cellulose. The depolymerization of cellulose and hemicelluloses via hydrolysis results in the cleavage of the glycosidic bonds and formation of simple sugars [8–14]. The main units are five-carbon sugars (xylose and arabinose) and six-carbon sugars (galactose, glucose, and mannose). These carbohydrates obtained from wood are valuable raw material for active compounds and intermediates for pharmaceuticals, food additives, cleaning agents, and others [5].

Although selective oxidation of sugars other than D-glucose has been investigated less intensively, L-arabinose and D-galactose obtained by hydrolysis of hemicelluloses (i.e., arabinogalactans), which appear in large amounts in larch species [13], can be selectively oxidized to arabinonic and galactonic acids, respectively. These aldonic acids are valuable in different industrial applications, for example, in the food industry, cosmetics, and medicine [15]. D-Galactose is another product of hydrolysis of arabinogalactans [13], which can be oxidized in a similar fashion.

Maltose and lactose are available in large amounts from renewable feedstocks, and their oxidation products are also of great interest for industrial applications. For example, lactobionic acid obtained from lactose is used as a complexing agent or as a component in organ transplantation preservation fluids and in anti-aging products. Therefore, oxidation of these sugars was studied more extensively [16–20].

Biomass-derived sugars and their derivatives are important organic platform molecules. Agricultural waste is an attractive feedstock for bioethanol production because lignocellulosic substances are both renewable and abundant. Efficient pretreatment for total delignification of lignocellulosics increases the concentration of fermentable sugars. Another way to make a process more cost effective is to develop novel fermentation technologies [21]. Selective oxidation of bioethanol/ethanol results in the formation of various valuable products, such as acetaldehyde, 1,1-diethoxyethane, acetic acid, and ethyl acetate. Acetic acid is a commodity used in many chemical syntheses including vinyl acetate production for further manufacturing of polyvinyl acetate.

Conversion of fructose and glucose to the potential platform molecule 5-hydroxymethyl-2-furfural (HMF) was successfully performed with high selectivity and sugar conversion [22–24]. HMF is the key molecule in the synthesis of several derivatives utilized in pharmaceuticals, antifugals, and polymers production. For example, HMF can be oxidized to 2,5-furandicarboxylic acid (FDCA), which is a possible replacement monomer for terephthalic acid utilized in production of polyethylene terephthalate (PET), the latter being the third most-produced polymer in the world [25].

Succinic acid (SA), which is currently produced by hydrogenation of maleic anhydride, could also be produced by fermentation of glucose. SA is considered to

be one of the 30 most promising biomass-derived products [26]. Selective hydrogenation of succinic ester, anhydride (SAN), and acid lead to the formation of γ-butyrolactone (GBL), 1,4-butanediol (BD), and tetrahydrofuran (THF), valuable as solvents or as a starting material for polymers, such as polyurethanes. In particular, GBL is an alternative to many chloro-containing solvents and is a starting material for pyrrolidone and pyrrolidone-derivatives synthesis, which in turn are widely used as industrial solvents, polymer building blocks, and intermediates for pharmaceuticals.

1.2.2 Extractives and Their Derivatives

1.2.2.1 Lignans

Lignans are a group of natural phenolic compounds found in different parts of plants, such as woody parts, roots, leaves, stems, seeds, flowers, and fruits. Coniferous trees contain a large number of different lignans in unconjugated form. The type and amount of lignan depend on the species and part of the tree. For example, Norway spruce (*Picea abies*) knots contain large amounts of lignans, among which hydroxymatairesinol (HMR) (4-[hydroxy94-hydroxy-3-methoxyphenyl)methyl]-3-(4-hydroxy-3-methoxybenzyl)dihydro-2(3H)-furanone) [27–29] is the most abundant one. Lignan HMR, constituting 65–85 wt.% of the total lignans, occurs in unconjugated free form [30], simplifying the isolation process.

Lignans were shown to provide benefits for human health. A lignan-rich diet, for example, decreases the risk for various cancers and cardiovascular diseases [31]. In addition to anticarcinogenic effects, lignans are proven to have antioxidative effects [32–34]. Evaluation of lignan's radical and superoxide scavenging activities have shown that lignan oxomatairesinol (oxoMAT) exhibits the highest superoxide scavenging activity. Therefore, lignan oxoMAT or its derivatives, due to their antioxidative activity [35] and UV-protection properties [36], can be applied for cosmetic and pharmaceutical uses (skin- and hair-care products), as well as color-retaining agents for the textile industry. However, oxoMAT cannot be extracted in considerable amounts from woody biomass, while it could be synthesized by selective oxidative dehydrogenation of HMR.

1.2.2.2 Fatty Acids

Tall oil is the by-product from the kraft pulping process. Crude tall oil (CTO) contains mainly fatty acids and resin acids, as well as sterols. Vacuum distillation of CTO produces the following products: tall oil fatty acids (TOFA) (16–30 %), tall oil resin (25–35 %), distilled tall oil (6–10 %), light oil (10–12 %), and pitch (20–30 %) [37]. The obtained from CTO fraction of TOFA contains fatty acids (C_6–C_{20}), where the main one is linoleic acid.

Linoleic acid is an unsaturated fatty acid. It is abundant in vegetable oils comprising safflower, grape seed, poppy seed, and sunflower oil. Linoleic acid (C18:2) has two double bonds located on carbons 9 and 12, both in *cis* configuration, and can be isomerized through double bond migration to conjugated linoleic acids (see Scheme 4.2). These isomers are well-known for their strong anticarcinogenic effect discovered in 1987 by Pariza and coworkers [38], as well as reducing body fat activity [39]. Health benefits are attributed to the presence of 9-*cis*,11-*trans* and the 10-*trans*,12-*cis* isomers [40–42].

Biodiesel manufacturing that utilizes transesterification of oils from biosustainable sources (mainly, rape-seed, and sunflower) produces large amount of glycerol as a by-product. For example, for each 9 kg of biodiesel produced, 1 kg of crude glycerol is formed as a side product according to data reported in [43]. At the same time, glycerol is an attractive multifunctional reactant for the production of a large number of valuable compounds. Many glycerol oxidation products are valuable intermediates for fine chemicals production.

Acetalization of glycerol with formaldehyde is another approach to convert glycerol into a more valuable substance. The product of this reaction, glycerol formal, has a wide application as a low-toxic solution for various injectable preparations, for binders and composites, in the synthesis of insecticides, in the formulation of water-based inks, and many others.

1.2.2.3 Resins

Naturally occurring styrene is a resin, which can be isolated from the Turkish tree, the Oriental sweetgum (*Liquidambar orientalis*). Styrene is a feedstock for various synthetic polymers, such as polystyrene, styrene-butadiene (SBR) rubber, styrene-butadiene latex. Epoxidation of styrene produces styrene oxide, which is used as a reactive plasticizer, a diluent for epoxy resins, and in the production of phenethyl alcohol and styrene glycol.

Turpentine is a fluid obtained by distillation of softwood tree resin. It is composed mainly of terpenes: α-pinene, β-pinene, and 3-carene depending on the tree species [44]. Isomerization of α-pinene to camphene is the first step in the industrial synthesis of camphor. The product is currently applied as a plasticizer for nitrocellulose, an antimicrobial substance, a flavoring in culinary preparations, and an active component in medical treatment.

Selective oxidation of α-pinene that is readily available from coniferous trees is of industrial interest. This process transforms inexpensive biomass-derived compounds into such chemicals as verbenol, verbenone, and α-pinene oxide, which are valuable in fine chemicals synthesis to produce flavors, fragrances, etc. [45].

Terpenes, which are extracted from biomass, are inexpensive renewable raw materials that have biological activity and are widely used in the development of new medicines. Likewise, the amination of alcohols to form complicated amines is of great importance in organic synthesis, granting access to valuable alkyl amines that are widely used as pharmacophores in numerous biologically

active compounds, dyes, agrochemicals, and functionalized materials. Myrtenol (6,6-dimethylbicyclo[3.1.1]hept-2-en-2-yl)methanol) and carveol (2-methyl-5-(1-methylethenyl)-2-cyclohexen-1-ol) are naturally occurring terpenes with primary and secondary alcohol groups, respectively. Amination of these alcohols results in the formation of building blocks for pharmaceuticals.

1.3 Gold Catalysts

Gold was generally regarded as an inert metal until the report of Haruta and coworkers, who first demonstrated catalytic activity of supported gold catalysts in low-temperature CO oxidation [46]. Remarkable activity of nanosized gold particles in oxygen-atom transfer reactions was further demonstrated in numerous selective oxidation reactions involving a variety of organic molecules, such as alcohols and aldehydes [47, 48], alkanes [49], olefins [50, 51], and polyfunctional alcohols [52–54]. The main advantage of gold-based catalysts is the utilization of molecular oxygen or air as oxidizing agents at relatively mild reaction conditions, which is an environmentally friendly approach to manufacturing organic chemicals. Moreover, compared to the more typically used platinum and palladium catalysts, gold is more stable in oxidative atmospheres and less sensitive toward poisons. However, the mechanisms of gold catalysis and, in particular, oxygen activation on gold are still a matter of debate. In [55], the catalytically active sites on gold are considered to be formed during the activation treatment of a gold precursor to form partially oxidized gold ($Au^{\delta+}$) atoms with unoccupied outer d-orbitals, similar to electronic structure of Pt. Thus, the formation of active centers via activation treatment is the result of electronic structure changes:

$$Au^{3+}d^8 6s^0 \text{ (precursor)} \longrightarrow activationAu^{\delta+}d^{10-\delta}6s^1 \text{ (catalyst)}$$
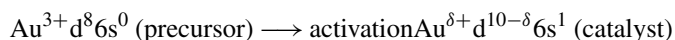
It is generally accepted that catalytic activity of gold catalysts depends strongly on gold particle size [56]. In [57, 58], it was emphasized that the largest activity is attributed to the presence of low-coordinated gold Au atoms, which are abundant on the smallest gold nanoparticles. The most reactive atoms are evidently located at the edges and corners of particles. These Au atoms are suggested to be able to facilitate adsorption of CO and O_2, thus catalyzing the CO oxidation reaction. The number of low-coordinated corner and edges sites decreases with increasing Au particle size. Therefore, even if the particle size changes rather slightly, the fraction of active sites can decrease significantly. In particular, the fraction of corners increases significantly when the particle size is less than 4 nm and scales approximately with d^{-3} as the diameter of the particle decrease (Fig. 1.1) [58]. Other effects, such as interaction with the support [59, 60], charge transfer [61], and strain [62] may also contribute to the activity of gold catalysts.

Activation of molecular oxygen on the gold particles is the crucial step in oxidation reactions. Low-temperature activation of oxygen in CO oxidation reaction was studied in [63]. The obtained results suggest that oxygen adsorbed on gold

Fig. 1.1 Calculated fractions of Au atoms at corners (*red*), edges (*blue*), and crystal faces (*green*) in uniform nanoparticles consisting of the top half of a truncated octahedron as a function of Au particle diameter. The *insert* shows a truncated octahedron and the position of representative corner, edge, and surface atoms. Reprinted from Ref. [58], Copyright © 2007, with permission from Elsevier
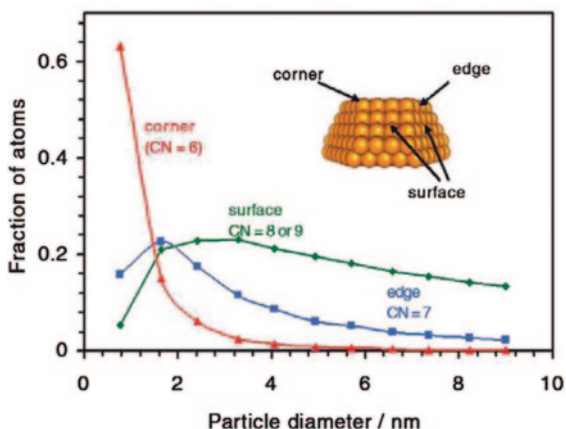
cluster to form superoxide (O_2^-), which is an activated form of oxygen. Moreover, it was also observed, that adsorbed oxygen enhances adsorption of substrate (CO) on the gold particles. A recent review of CO oxidation over gold catalysts can be found in Ref. [64].

Gold catalysts were also evaluated in other types of reactions. For example, the selective hydrogenation of olefins and dienes was first illustrated by Bond et al. [65]. Since gold is less active in hydrogenation than conventional transition metal catalysts as Pt, Pd, Ni (and number of other metals), Au catalysts were found to be more selective in hydrogenation reactions of molecules with several reducible groups. Gold catalysts were shown to be active and selective in hydrogenation of various molecules, such as olefins and dienes [65], as well as the carbonyl group of α-β-unsaturated aldehydes [66, 67], and nitro groups [68].

The unique properties of nanosized gold to activate oxygen, act as Lewis acid, and facilitate weak binding of hydrogen allows gold catalysts to be successfully employed in an extended number of fine chemicals synthesis reactions such as isomerization, acetalization, and amination involving 'borrowing hydrogen' step. Gold as a catalyst can be applied in similar transformations of biomass-derived compounds into value-added chemicals.

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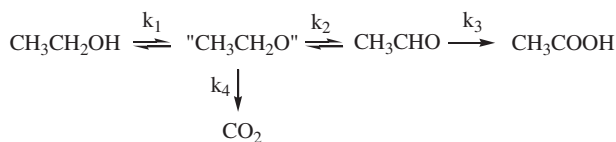68. A. Corma, P. Concepcion, P. Serna, Angew. Chem. Int. Ed. **46**, 7266 (2007)

Chapter 2
Selective Oxidation/Dehydrogenation Reactions

2.1 Primary Alcohol and Aldehyde Oxidation

2.1.1 Ethanol Oxidation

Selective oxidation of ethanol results in the formation of acetaldehyde, 1,1-diethoxyethane, acetic acid, and ethyl acetate. Currently, 75 % of acetic acid is formed via methanol carbonylation utilizing fossil resources and 25 % by classical fermentation [1]. Ethyl acetate has a wide range of applications in different areas including the paint and food industries [2]. Gold catalysts were found to be active and selective in the synthesis of both acetic acid and ethyl ester in the presence of oxygen [3, 4]. Moreover, the use of gold catalysts allowed for the use of less severe reaction conditions compared to those needed for other catalysts active in the gas-phase such as supported V_2O_5 (175–200 °C, 270 kPa), Nb-Mo-V-Ox (237 °C, 1600 kPa) [5–7]. It is important to note that the product composition depends on the reaction conditions employed as well as the nature of the catalysts, including the metal particle size and the composition of the support.

Aerobic oxidation of aqueous ethanol to acetic acid over $Au/MgAl_2O_4$ and Au/TiO_2 was studied by Christensen and coworkers [3, 4]. For both catalysts, the yield of acetic acid was over 90 % at high ethanol conversion. The reaction was performed at 150 °C, under technical air pressure of 3.5 MPa. The kinetics of acetic acid formation were investigated and were consistent with the following proposal regarding the reaction mechanism. As a first step, ethanol is adsorbed on the gold surface to form activated intermediate species, which then is oxidized/dehydrogenated to the aldehyde. Consequently, aldehyde is oxidized to acetic acid, while CH_3CH_2O can also undergo C–C bond cleavage to produce CO_2 (Scheme 2.1). The selectivity was influenced by the ethanol concentration. At ethanol concentration lower than 60 wt. %, the major product was acetic acid, whereas when the concentration exceeded 60 wt. %, the selectivity shifted towards ethyl acetate [4].

$$CH_3CH_2OH \underset{\xrightarrow{k_1}}{\rightleftharpoons} \text{"}CH_3CH_2O\text{"} \underset{\xrightarrow{k_2}}{\rightleftharpoons} CH_3CHO \xrightarrow{k_3} CH_3COOH$$

$$k_4 \downarrow$$

$$CO_2$$

Scheme 2.1 The reaction pathway of ethanol oxidation over Au catalysts. Reprinted from Ref. [3], Copyright © 2007, with permission from Elsevier

Oxidation of alcohols over gold catalysts at temperatures lower than 150 °C is typically performed in the liquid-phase [8–11]. However, a solvent-free reaction is more attractive from industrial point of view. The reaction temperatures currently used for selective oxidation of gas-phase ethanol are generally above 200 °C over various Au catalysts, which leads to catalyst deactivation. Therefore, the low-temperature activity of Au/TiO_2 catalysts in gas-phase ethanol oxidation observed in [12] seems to be promising for practical application. A so-called 'double peak' catalytic activity was observed only in case of titania-supported gold catalyst and represents the unusual activity in gas-phase at 120 °C and the expected one at temperature above 200 °C (Fig. 2.1).

To understand the catalytic function of gold, the mechanism of gas-phase oxygen activation was studied by oxygen isotope exchange (OIE) technique by Sobolev et al. [13]. The low-temperature activity of the catalyst in homo-exchange can indicate the involvement of very active surface oxygen species. It should be noted that Au/TiO_2 and Au/Al_2O_3 have demonstrated similar activity in ethanol dehydrogenation at low temperature (75 °C), while Au/SiO_2 was not active at the same conditions. Interactions of Au/TiO_2 surface oxygen atoms with hydrogen from the gas-phase resulted in the formation of water at 150 °C. Furthermore, Au/TiO_2 pretreated in hydrogen is able to catalyze oxygen isotope homo-exchange at room temperature, while the equilibrium of the exchange can be reached in a few minutes. Similar to Au/TiO_2 catalyst Au/Al_2O_3 has demonstrated activity

Fig. 2.1 Ethanol conversion over TiO_2 (*filled triangle*), 2 wt. % Au/TiO_2 (*filled circle*), 2 wt. % Au/Al_2O_3 (*filled square*), 1 wt. % Au/SiO_2 (*filled diamond*). Reprinted from Ref. [12], Copyright © 2010 Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim
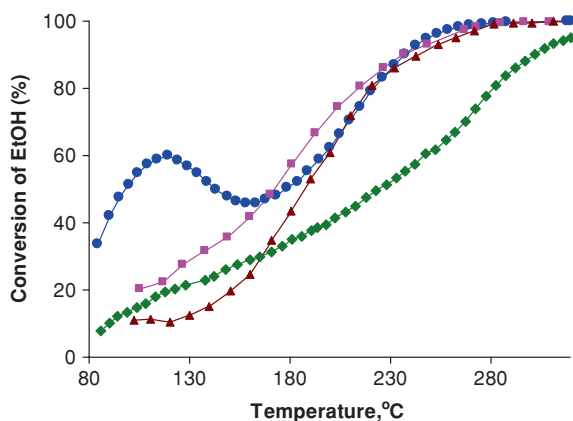
in oxygen isotope homo-exchange, although not significant. In the studied reaction Au/SiO$_2$ was not active at all. Catalyst pretreatment by molecular hydrogen led to formation of active oxygen species on the surface of titania and alumina. Although the exact nature of these species is unclear, they might be O$^-$ anion radicals or O$_2^-$ superoxide ions. The thermal stability of these species on Al$_2$O$_3$ is much lower than those on TiO$_2$. It was assumed that formation of surface oxygen species and their stability are the key factors responsible for the differences in catalyst performance among the various supported samples and higher catalytic activity of Au/TiO$_2$ at low temperature. Moreover, the activity of titania-supported gold in ethanol dehydrogenation allows additional in situ hydrogen formation thus enhancing oxidizing surface species formation. The thermostability of active oxygen species was estimated based on the temperature dependence of the oxygen isotope homo-exchange rate, which is proportional to the amount of active surface oxygen. In contrast to Al$_2$O$_3$, TiO$_2$ surface provides the essential thermostability of the generated oxygen species.

Structure sensitivity and kinetics of ethanol oxidative dehydrogenation in aerobic and anaerobic conditions were thoroughly studied by Guan et al. [14]. Silica-supported gold catalysts (with and without aluminum impurities) were applied in the temperature range 150–400 °C. The gold particle size was varied between 1.7 and 15 nm. Ethanol dehydrogenation had a selectivity of 100 % at temperatures below 350 °C, and was still over 90 % at 400 °C. The highest activity per exposed site was obtained over a gold catalyst with a metal particle size of about 6 nm. The calculated turnover frequency (TOF) for ethanol dehydrogenation at 250 °C was 350 h^{-1} while the achieved selectivity to acetaldehyde was 95 % at a conversion of 90 %. The presence of molecular oxygen significantly promoted the reaction rate and lowered the apparent activation energy. The TOF of oxidative dehydrogenation was four times higher (1300 h^{-1} at 200 °C). Catalytic activity dependence on the particle size was also different and increased with increasing particle size up to 10 nm (Fig. 2.2). Selectivity to acetaldehyde was 90 % at about 100 % of ethanol conversion.


Fig. 2.2 Turnover frequency (TOF) for ethanol dehydrogenation in the absence (*filled square*, 250 °C) and presence (*filled triangle*, 200 °C) of oxygen as a function of the gold particle size. Reprinted from Ref. [14], Copyright © 2009, with permission from Elsevier
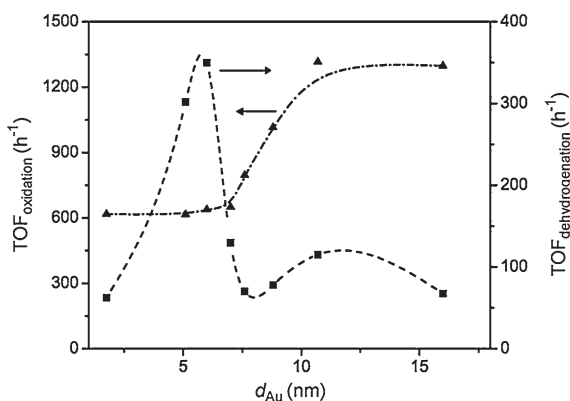
2.1.2 5-Hydroxymethyl-2-Furfural Oxidation

The selective oxidation of HMF was studied over various catalysts such as Pt–Pb, Pt/Al$_2$O$_3$, Pd, metal bromide catalysts (Co/Mn/Zn/Br), vanadyl-pyridine complexes [15–18]. In general, FDCA production proceeds in two stages: first, the aldehyde group is oxidized to 5-hydroxymethyl-2-furancarboxylic acid (HFCA), and consequently FDCA is formed from the primary alcohol group oxidation (Scheme 2.2). Typically, the first stage is much faster than the second one. Another detected intermediate is 5-formyl-2-furancarboxylic acid (FCA). Catalysts based on transition metals can be deactivated due to over oxidation of the metal surface. In case of nontransition metals as catalysts the main product was reported to be 2,5-diformylfuran (DFF) with selectivity of 99 % at mild temperature (50–75 °C) and FDCA with selectivity higher than 97 % and yield of ca. 60 % at higher temperatures (100–225 °C). Notably, basic pH is favorable for FDCA production.

Since oxidation of HMF to FDCA is in fact selective oxidation of two groups: primary alcohol and aldehyde, where gold catalysts have demonstrated high activity and selectivity, several attempts to apply Au catalyst were reported. Oxidation of HMF over Au/TiO$_2$ in methanol at 130 °C in the presence of base was reported by Taarning et al. [19]. Gorbanev et al. [20] also reported utilization of Au/TiO$_2$ at 30 °C, while the reaction was performed in aqueous solutions with NaOH to HMF molar ratio of 20. Increasing oxygen pressure from 1000 to 2000 kPa boosted the FDCA yield up to 71 % at full HMF conversion. Selective oxidation of HMF in
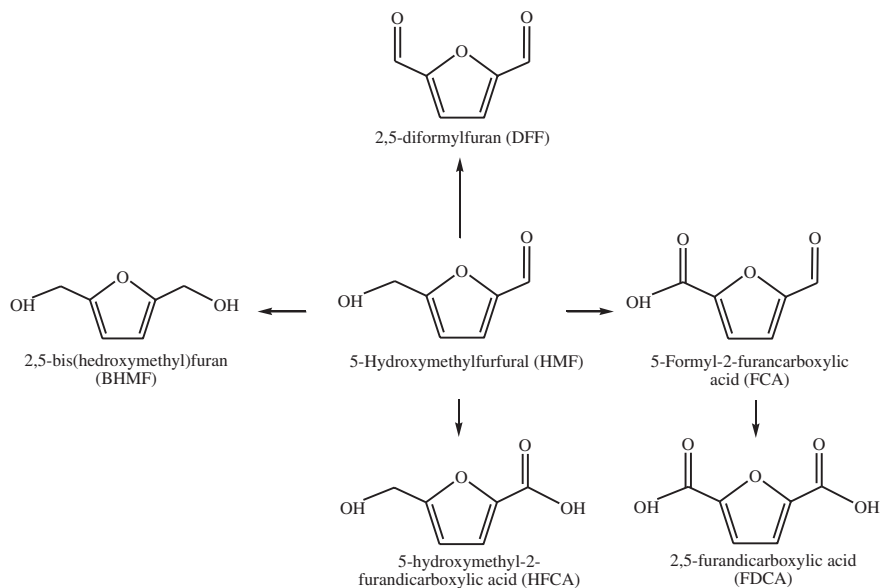
Scheme 2.2 Products of HMF oxidation. Reprinted from Ref. [22]. Copyright © 2011, with permission from Elsevier

aqueous solutions was investigated over Au/TiO$_2$, Au/CeO$_2$, Au/C, Au/FeO$_2$ by Casanova et al. [21]. In this series of catalysts the best results were obtained over Au/TiO$_2$ and Au/CeO$_2$ catalysts. The yield of FDCA was more than 99 % after 8 h over Au/CeO$_2$. The optimized reaction conditions were found to be 130 °C, 1000 kPa oxygen, and the NaOH to HMF molar ratio equals to 4.

Recently, Davis et al. have compared the reaction rate and product distribution for HMF oxidation over supported metal catalysts: Pt/C, Pd/C, Au/C, Au/TiO$_2$ [22]. Pt and Pd were able to oxidize HFCA to FDCA, but gold catalysts demonstrated one order of magnitude higher reaction rate (1.6–5.0 s^{-1}) at the same conditions of 22 °C, 690 kPa of oxygen. The major product over the gold catalyst was HFCA. At the same conditions, increasing the base concentration (OH$^-$) improved the selectivity towards FDCA formation.

The oxidation of HMF over a hydrotalcite-supported gold nanoparticle catalyst (Au/HT) in water at 95 °C under atmospheric oxygen pressure without addition of homogeneous base was recently demonstrated [23]. This study reported the oxidation as an environmentally benign process, which could be operated even at 95 °C using a conventional glass reactor with atmospheric oxygen flow. Since HT consists of layered clays with HCO$_3^-$ and OH$^-$ groups on the surface, it is known to exhibit high activity for base-catalyzed reactions. However, the potential for leaching of the solid base exists so the support might act as a substitute for homogeneous base in promoting catalyst activity [24].

Bimetallic Au–Cu catalysts supported on titania display higher activity compared to monometallic Au [25]. In this study the influence of base content, catalyst metal loading, temperature, and reaction time was investigated using Au–Cu/TiO$_2$ catalyst. It was also demonstrated that, in the absence of any catalyst, addition of base resulted in HMF degradation to form levulinic and formic acid, while in the presence of catalyst and base HMF was exclusively oxidized to HFCA and, subsequently, to FDCA. Under the optimized reaction parameters yield of FDCA was 90–99 % after 4 h at 95 °C at base loading corresponding to NaOH to HMF molar ratio of 4.

The significant role of OH-groups in the reaction mechanism was pointed out by further investigation [26]. Experiments conducted with labeled oxygen and water (^{18}O$_2$, H$_2$^{16}O and H$_2$^{18}O) indicated that namely oxygen atoms (^{16}O and ^{18}O) in water were incorporated into the HMF oxidation products (HFCA and FDCA), while gaseous oxygen atoms were not found in the products. One of the explanations of the oxygen role is indirect participation in the oxidation reaction. The oxygen from the gas-phase is adsorbed on the metal surface and reduced by electrons deposited into the metal during adsorption and reaction of hydroxide ions to form peroxide species and, consequently, hydroxide ions (see Scheme 2.3).

Synthesis of FDCA is challenging due to its low solubility in most industrial solvents [27]. This difficulty can be overcome by synthesis of FDCA ester, i.e., dimethylfuroate (DMF), which is soluble in most commonly applied solvents. Casanova et al. have demonstrated excellent activity and selectivity of Au/CeO$_2$ catalyst in aerobic HMF oxidation to the alternative product (DMF) in base-free conditions [28].

HMF Oxidation Scheme
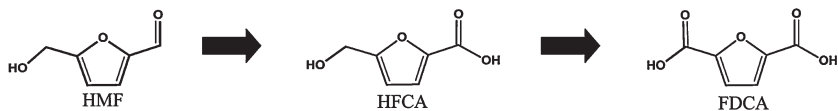
HMF Oxidation Mechanism
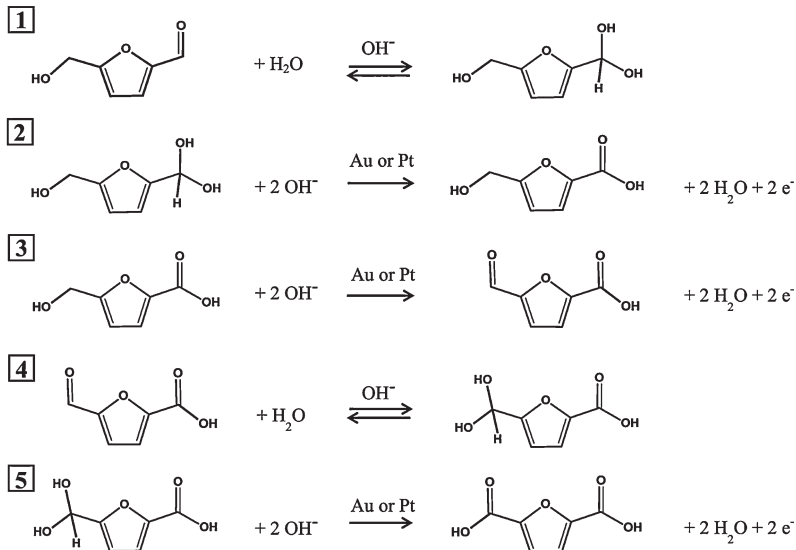
Scheme 2.3 Overall reaction scheme and proposed mechanism for the oxidation of HMF in aqueous solution in the presence of excess base (OH⁻) and either Pt or Au. Dioxygen (not shown) serves as a scavenger of electrons that are deposited into the metal particles during the catalytic cycle. Reproduced from Ref. [26] with permission from The Royal Society of Chemistry

2.1.3 Selective Oxidation of Sugars

Heterogeneous catalytic oxidation of sugars over gold catalysts is very attractive, since these catalysts have demonstrated high activity and selectivity. Utilization of gold catalysts has an environmental advantage—the reaction can be performed using air or molecular oxygen as an oxidizing agent at mild reaction conditions (30–90 °C).

2.1.3.1 Selective Oxidation of Glucose

Since D-glucose is the most abundant monosaccharide in nature, its oxidation to D-gluconic acid was extensively investigated [29, 30]. The optimal conditions for D-gluconic acid formation were found to be 50 °C at pH 9.5 and 60 °C at pH 7.0 (Fig. 2.3), while reaction at higher temperatures and pH values resulted in formation of such side products as fructose, sorbitol, mannose, glycolaldehyde, and

Fig. 2.3 Initial reaction rates of D-gluconic acid formation at different reaction temperatures and pH values. Reprinted from Ref. [31], Copyright © 2004, with permission from Elsevier
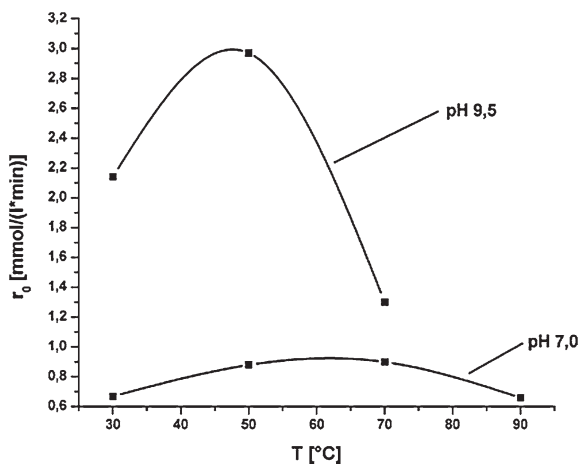
maltose [31]. Kinetic studies on glucose selective oxidation resulted in different conclusions on the reaction mechanism. In [31] the reaction rate was independent of glucose concentration. However, further investigation showed the reaction rate to increase with increasing oxygen pressure from 1.5 to 9 bar and to depend on glucose concentration, having maximum at 20–30 wt. % [32]. The results fitted a Langmuir–Hinshelwood model. In another study [33] the reaction rate was found to be proportional to the oxygen pressure and increased with glucose concentration, with the energy of activation studied in the absence of mass transfer limitations estimated to be 47 kJ/mol. This value is in the same range as one reported later in [32]. According to considerations in [33], the reaction follows the Eley–Rideal mechanism, where an oxygen molecule from the fluid phase reacts directly with chemisorbed glucose.

Structure sensitivity of D-glucose oxidation to D-gluconic acid was studied in [31]. Au/C catalysts were prepared by gold sols immobilized onto a carbon support. Supported gold particles had a mean diameter of Au particles 3–6 nm with a gold loading of 0.4–0.7 wt. %. Catalytic activity of Au/C was found to have an exponential dependence on the gold specific surface area.

High selectivity of gold colloids in the oxidation of D-glucose to D-gluconic acid was demonstrated by Prüße and co-workers [34, 35]. Under the same conditions, Au/TiO2 catalyst prepared by deposition–precipitation with urea (DPU) demonstrated the best performance corresponding to the complete glucose conversion with selectivity to gluconic acid of 98 %, and the specific catalytic activity of 236 $mmol_{glucose} \, min^{-1} g_{metal}^{-1}$ [34]. Development of gold on alumina catalyst preparation methods revealed a possibility to support Au particles having less than 2 nm in diameter by an incipient wetness method (IW), which has advantages over the DPU method from ecological and economical points of view. Application of 0.3 wt. % Au/Al_2O_3 catalyst prepared by IW in glucose oxidation resulted in complete selectivity to sodium gluconate with the catalyst specific activity of 1100

$mmol_{glucose}$ $min^{-1}g_{metal}^{-1}$ [36]. An advanced catalyst preparation technique was shown by the group of Haruta to improve Au catalyst performance [37], where gold supported on ion-exchange resins exhibited a TOF of 7.5 s^{-1} in glucose oxidation reaction at 60 °C and pH 9.5. Catalytic activity was found to increase with increasing basicity of ion-exchange resins. Relatively high catalytic activity in glucose oxidation (TOF of 11 s^{-1}) was obtained over Au/C catalysts prepared by a direct contact of gold precursor with support by grinding of carbon [38] and cellulose [39] with dimethyl Au(III) acetylacetonate. The nature of the support was found to play an important role. In [40], Au catalysts supported on TiO_2, SiO_2, CeO_2 were studied. Since glucose is a large multifunctional molecule, different surface arrangements and sites are needed for its adsorption. Therefore, in this series of catalysts, gold supported on silica with a mean size of gold particles ca. 10 nm was the most active catalyst [40].

Hydrogen peroxide as an oxidizing agent was investigated in [41]. In this study D-glucose oxidation by H_2O_2 was performed over 0.3 wt. % Au/Al_2O_3 at relatively mild conditions (40 °C, pH of 9). The investigation revealed that the oxidizing species were formed via H_2O_2 decomposition over the gold catalyst. Similar to aerobic oxidation reported in [32] the apparent energy of activation was 48 kJ/mol, and the reaction order for D-glucose was 0.5. In general, oxidation by hydrogen peroxide seems to be similar to aerobic oxidation, as the oxygen from gas-phase was observed to form peroxide-like species promoting oxidation.

2.1.3.2 Selective Oxidation of Arabinose, Galactose and Other Sugars

The selective oxidation of arabinose to its corresponding carboxylic acid (arabinonic acid) was studied in [42, 43]. The reaction (see Scheme 2.4) was performed at relatively moderate conditions, using oxygen as an oxidant [43]. Gold catalyst did not show any activity decline or decrease of selectivity to the desired product. It was confirmed that pH is one of the most crucial factors in the oxidation of arabinose to arabinonic acid. Generally, at low pH, the product adsorption on the catalyst strongly inhibits the reaction; therefore, the reaction is performed in the presence of base to increase the rate of the oxidation. Thus, in [43] the increase of pH value from 6 to 9 resulted in the corresponding arise of TOF from 0.015 to 0.206 s^{-1}. However, increasing of pH resulted in gold leaching from the catalyst
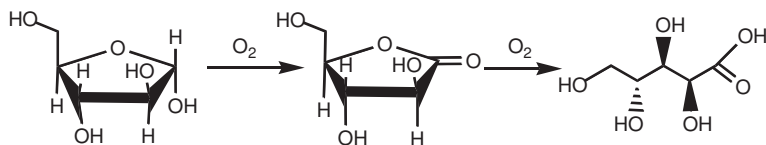
Scheme 2.4 Reaction scheme for the selective oxidation of arabinose to arabinogalactan and arabinonic acid by molecular oxygen. Reprinted from Ref. [43]. Copyright © 2010, with permission from Elsevier

and decrease of selectivity toward the reaction intermediate, as well as formation of by-products, which inhibit the reaction. Catalyst activity and conversion of arabinose increase as the pH increases from 6 to 9, indicating that slightly alkaline media, i.e., pH 8, is favorable. The kinetic experiments revealed as well an increase of the reaction rate with increasing of oxygen flow rate from 2.5 ml/min to 5.0 ml/min. The apparent activation energy was estimated to be ca. 24 kJ/mol in the absence of mass transfer limitations. The reaction kinetics was comprehensively studied in [44].

The influence of the catalyst support and active phase was studied in [43, 45]. The support nature and catalyst pretreatment affect the catalytic properties. Bimetallic Au–Pd catalysts demonstrated higher activity and selectivity compared to monometallic Au and Pd catalysts. The synergetic effect is attributed to the activation of arabinose by Au species, while Pd species can provide activation of oxygen.

The rate of the reaction of arabinose oxidation to arabinonic acid is apparently structure sensitive (Fig. 2.4). Dependence of catalytic activity on gold particle size has a volcano relationship with a maximum at gold cluster size ca. 2 nm. The data were also described quantitatively [46] based on a thermodynamic approach. Since the kinetic data is attributed to the average cluster size, limitations of the applied calculations are related mainly to the accuracy of the Au cluster size determination. However, the results of the calculations confirmed a good correspondence between the experimental data and the model.
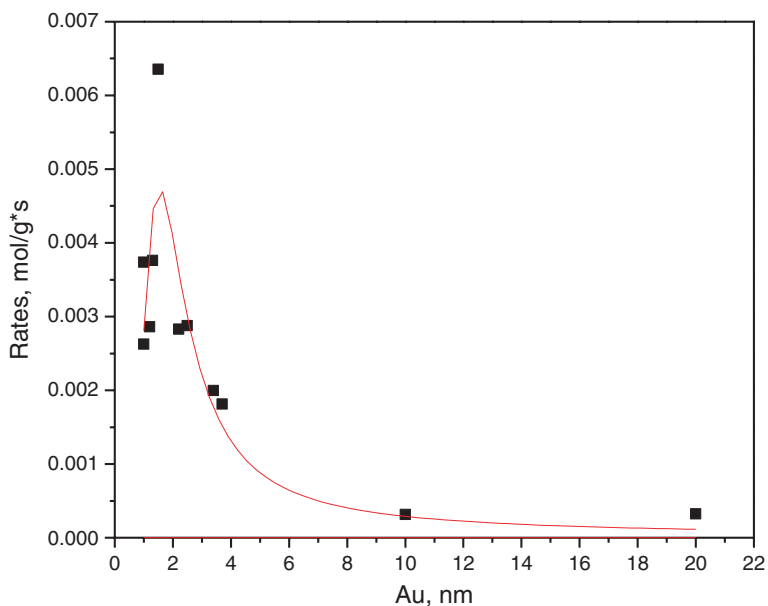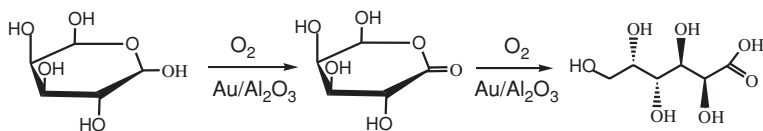

Fig. 2.4 Dependence of initial rates in arabinose oxidation on the particle size of Au/Al_2O_3 catalysts. Reprinted with permission from Ref. [46]. Copyright © 2011, American Chemical Society

Scheme 2.5 The reaction pathway of D-galactose selective oxidation over Au catalyst. Reprinted from Ref. [47], Copyright © 2011 Wiley–VCH Verlag GmbH & Co. KGaA, Weinheim

Gold catalysts exhibit high catalytic activity in the selective oxidation of D-galactose to galactonic acid (Scheme 2.5), although this reaction was not intensively investigated. In [47] the reaction was performed in a semi-batch reactor at 60 °C, under pH-s and constant oxygen flow. The reaction is structure sensitive, with Au particles of the size of 2.6 nm exhibiting the maximum activity. Similar to the case of glucose oxidation [30], alkaline conditions (pH of 8–10) accelerate the reaction rate and increase the reaction selectivity to galactonic acid, although at higher pH > 10 sugar degradation can be observed.

Other carbohydrates can be also oxidized to valuable aldonic acids over gold catalysts. The selective oxidations of various monosaccharides (ribose, xylose, lyxose, mannose, rhamnose, galactose, N-acetyl-glucosamine) and disaccharides (lactose, maltose, cellobiose, melibiose) over gold catalysts were studied in [42]. Gold catalysts demonstrated higher selectivity (ca. 100 %) to corresponding aldonic acids and higher specific catalyst activity (6–24 mmol/min × g_{Au}) compared to palladium and platinum catalysts (1–10 mmol/min × $g_{Pt\ or\ Pd}$) applied in the same conditions. Similar to selective oxidation of glucose and arabinose, in order to avoid molecules degradation and formation of by-products, it is preferable to conduct the reaction at low temperatures (40–60 °C) and in light alkaline media at pH 7–9.

Structure sensitivity of lactose selective oxidation to lactobionic acid (Scheme 2.6) was studied. Similar to arabinose and galactose the dependence of the reaction rate on Au particle size has volcano shape with maximum at 6 nm [48]. Support does not influence the reaction selectivity. In [42] it was reported that Au/TiO$_2$ (gold particle size 1–2 nm) is more active in mannose oxidation, while Au/Al$_2$O$_3$ is more active in lactose oxidation.

2.2 Secondary Alcohols Oxidation

The formation of the lignan oxoMAT from the lignan HMR by light-irradiation was reported in [49], while in [50] 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) was used as an oxidizing agent. An attempt has been made to perform the reaction via heterogeneous catalysis, namely Pd/C, providing a more commercially attractive synthesis of oxoMAT. However, oxoMAT was not the only product in this reaction [51]. OxoMAT is formed via selective oxidative dehydrogenation of secondary
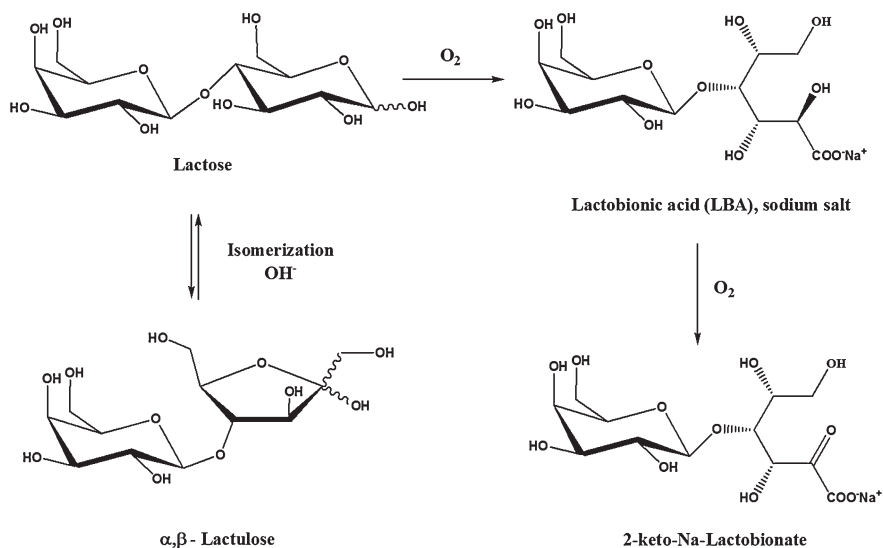
Scheme 2.6 The lactose oxidation over gold catalyst by molecular oxygen in the presence of base. Reprinted from Ref. [96], Copyright © 2008, with permission from Elsevier
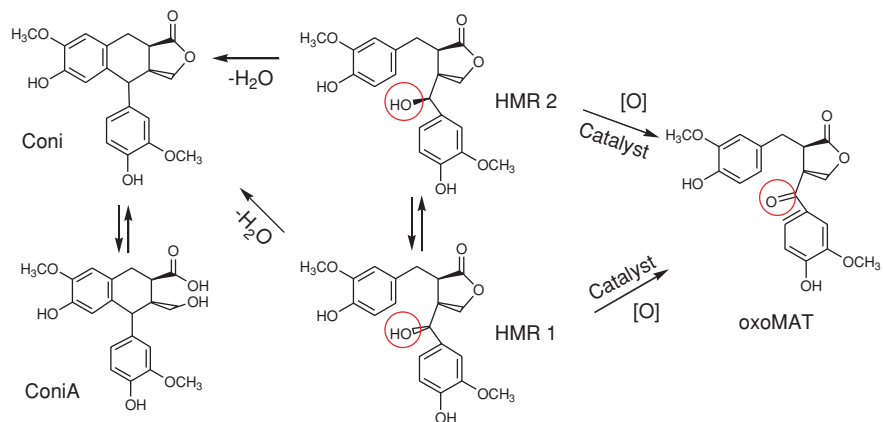
Scheme 2.7 Reaction pathways of lignan hydroxymatairesinol (HMR) transformation over Au gold catalysts to the lignans α-conidendrin (Coni), α-conidendric acid (ConiA) and oxomatairesinol (oxoMAT). Reprinted from Ref. [53]. Copyright © 2012, with permission from Elsevier

alcohol according to the reaction network presented in Scheme 2.7. Application of heterogeneous Au catalysts was demonstrated for the first time in [52]. Gold catalysts boost the selectivity to oxoMAT up to 100 %. At the same conditions, conversion of HMR over palladium catalysts was lower than over gold ones.

Monometallic Au and bimetallic Au–Pd catalysts supported on various carriers (Al_2O_3, TiO_2, MgO, SiO_2, C, La_2O_3, CeO_2, ZrO_2), zeolites, and mixed oxides (Al_2O_3–CeO_2, Al_2O_3–CeO_2–ZrO_2) were tested in the oxoMAT synthesis [53]. Gold catalysts exhibited a TOF to be in the range of 0.007–0.117 h^{-1}, while among all tested catalysts Au/Al_2O_3 has shown the highest activity (TOF of 0.117 h^{-1}). Au/Al_2O_3, TiO_2, SiO_2, C have demonstrated 100 % selectivity towards oxoMAT. Reaction over Au/La_2O_3, CeO_2, ZrO_2 catalysts led to the formation of the other lignans such as α-conidendrin, α-condendric acid, and isomerization between HMR isomers. Addition of Pd did not improve the catalyst performance, the initial catalytic activity was found to be similar for mono and bimetallic catalysts. The role of the support was found to have a dominating effect on the reaction selectivity. Thus, gold supported on basic supports was less active and selective to oxoMAT, than on acidic ones. High catalytic activity was attributed to the presence of OH-groups on the support surface formed due to water adsorption on Lewis acid sites [52, 53].

HMR extracted from wood biomass is a mixture of two diastereomers: (7R,8R,8′R)-(-)-7-allo-hydroxymatairesinol (HMR 1) and (7S,8R,8′R)-(-)-7-allo-hydroxymatairesinol (HMR 2), which exist in different conformations [54] and can be isomerized into each other. The molar ratio SRR-HMR/RRR-HMR depends on the tree species and in case of Norway spruce (*Picea abies*) knots typically is 2 mol/mol. Both isomers can be oxidized into oxoMAT over Au catalysts, while SRR-HMR is the most reactive one. The difference in the oxidation rate of each isomer was explained by possible steric hindrance and difference in the isomers energies confirmed by use of quantum chemical calculations in [55].

Synthesis of oxoMAT can be performed under aerobic and anaerobic conditions. However, the presence of oxygen significantly increases the reaction rate [52]. The reaction mechanism of aerobic and anaerobic HMR dehydrogenation was investigated [55]. Activated oxygen was found to play the essential role in the reaction, as oxygen species on the gold catalytic surface, which act as Brønsted basic sites, enhance the dehydrogenation rate [56].

A kinetic study of lignan HMR aerobic dehydrogenation was performed. The reaction order was found to be ca. 0.3–0.4 order in respect to HMR isomers and oxygen. The apparent energy of activation was estimated to be 43 kJ/mol [57]. The kinetic model of the reaction was developed. During the process the reaction rate was found to be retarded by the formed oxoMAT and impurities presented in the substrate, which was included in the model. The deactivation of the catalyst was studied in details in [58].

2.3 Polyalcohol Oxidation

Glycerol is a multifunctional molecule, and the oxidation pathway is complicated by parallel and sequential reactions (Scheme 2.8). Glyceraldehyde can be easily isomerized to dihydroxyacetone, while the oxidation of the former one is more
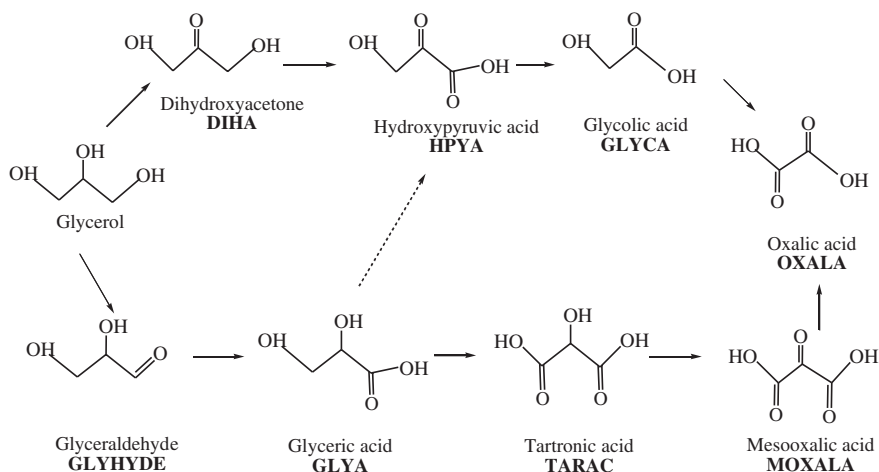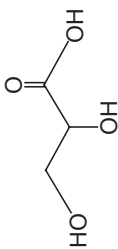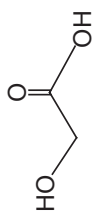
Scheme 2.8 The reaction pathway of glycerol selective oxidation. Reprinted from Ref. [84]. Copyright © 2006, with permission from Elsevier

challenged and, thus, glyceric acid is the major product in many cases. Traditional catalysts based on Pt and Pd can be deactivated due to overoxidation of their surface. However, gold catalysts were found to be more stable than Pt and Pd, and possess high selectivity. Reaction over gold catalysts can lead to products with one or two carbon atoms, as for example, glycolic acid. Subsequent oxidation of glyceric acid results in tartronic acid formation. Catalyst composition and reaction conditions were found to affect the product selectivities [59–64].

Hutchings and co-workers reported the formation of glyceric acid at selectivity of 100 % over Au/C in autoclave under 3–6 atm of oxygen, at 60 °C, while the selectivity was decreasing to 86 % at increasing of glycerol conversion from 56 to 72 % [59, 60]. In the presence of base the group of Prati observed the selectivity depends on a combination of catalyst properties, including metal type, Au particle size and support properties [61–64]. In their further study the experimental conditions were optimized [65]. The highest selectivity to glycerate was 92 % at full glycerol conversion at 30 °C under 300 kPa of oxygen and NaOH/glycerol molar ratio of 4. Furthermore, it was found, that catalysts with average Au particles size about 6 nm did not maintain the initial selectivity at full conversion, while larger particles (> 20 nm) showed constant selectivity during the reaction.

In the last years the number of papers on glycerol oxidation with oxygen is essentially increased. Gold catalyzed oxidation of glycerol using H_2O_2 as an oxidant was as well successfully performed in [66]. In this case glycolic acid was the major product (ca. 60 % yield). In Table 2.1 the reaction conditions, catalyst selection, and selectivity to different products are given based on the results published recently [67–82]. Different aspects of glycerol oxidation such as the effect of reaction conditions, catalyst, support nature, Au particle size as well as reported kinetic peculiarities discussed bellow.

Table 2.1 Selective oxidation of glycerol. Catalyst selection, reaction conditions, product selectivity at given glycerol conversion

Product	X (%)	S (%)	Reaction conditions	χ mol/mol (or pH)	Catalyst	d_{Me} (nm)	TOF (h^{-1})	References
Glyceric acid	40	45	60 °C, 100 kPa (O_2)	pH 12	Au/C, TiO₂, Al₂O₃, MgO, CeO₂	2–5		[68, 85]
	10–80	50–70	35–60 °C, 1000 kPa (O_2)	2	Au/C, TiO₂,	2–12	100–1090	[74, 85]
	12–97	52–78	50 °C, 100–600 kPa (O_2)	0.5–4	Au–Pd/C	3.7		[79]
	50	62–83	60 °C, 500–1000 kPa (O_2)	2	Au/C	5–42	61200	[75]
	50–100	50–77	30–50 °C, 300 kPa (O_2)	4	Au–Pd/C			[71, 72]
	70–90	62	50 °C, 300 kPa (O_2)	4	Au–Pt/C	2–3	980	[73, 76]
	50	65–84	60 °C, 1000 kPa (O_2)	2	Au–Pd/C, Au/C	3–5	18000–61200	[78]
	30	40–100	60 °C, 100–300 kPa (O_2)		Au/C			[80]
	13–78	30–55	60–90 °C, 600 kPa (O_2)	2	Au/C, TiO₂, Nb₂O₅	5	2500–4310	[82]
	70–90	40–60	60 °C, 300 kPa (O_2)	2	Au/C			[89, 92]
	100	60	H_2O_2		Au/C			[67]
	10–80	20–50	35–60 °C, 1000 kPa (O_2)	2	Au/C, TiO₂	5–12	18000–61200	[74]
Glycolic acid	50	55–60	60 °C, 300 kPa (O_2)	0.5–2	Au/C	5–23	1080–4000	[6]
	50	36	60 °C, 100 kPa (O_2)	pH 12	Au–Pt/C			[76]
Dihydroxyacetone	93	60	60 °C, 300 kPa (O_2)	2	Au/C	5	4240	[89]

X glycerol conversion; S selectivity towards the product; d_{Me} average diameter of the supported metal; χ NaOH to glycerol molar ratio

2.3.1 Role of Base

The presence of a base is essential for glycerol oxidation. According to a commonly accepted opinion, bases promote dehydrogenation step of glycerol oxidation/dehydrogenation [6, 59, 67]. The reaction selectivity can be controlled by the amount of base. As shown in [67] the selectivity to glyceric and tartronic acid could be changed by the base amount. Glyceric acid formation was favored up to NaOH/glycerol molar ratio of 2, although with increasing of this ratio to 4, tartronic acid (product of further glyceric acid oxidation) was formed with high selectivity. At the same time the reaction rate was enhanced by increasing of base loading up to a molar ratio NaOH/glycerol of 2 and above this ratio almost did not change. Similar observation was made by the group of Prati [76].

2.3.2 Gold Particle Size Effect

The structure sensitivity of the reaction was studied by several research groups. For this purpose size of Au particles supported on carbon was varied in the range 2–45 nm [67] and 5–42 nm [82]. The results obtained in both works are similar. The smallest Au particles have demonstrated much higher activity in glycerol oxidation. However, the selectivity to glyceric acid at conversion of 30 % passed through a maximum: increased with increasing of Au particle size, reached maximum at average Au diameter 3.7 nm (75 % to glyceric acid) and followed by decreasing of selectivity to glyceric acid with increasing of Au particles size up to 42 nm. Furthermore, the smallest particles have the highest selectivity to glycolic acid—the product of C–C bond cleavage [67]. The reason for this was revealed in [74], where Ketchie et al. have observed that highly dispersed gold particles are more active in hydrogen peroxide formation during glycerol oxidation, which in turn promotes C–C cleavage. Influence of gold particle size on catalyst activity and selectivity was also evaluated using gold supported on carbon nanotubes (Au/CNT) with Au particles size 3–23 nm [82]. Dependence of turnover frequency (TOF) on gold particle size has a maximum at 5.5 nm at TOF value of $6 \pm 2.1 \times 10^{-3}$ h^{-1}. Catalyst supported on multi-walled carbon nanotubes (Au/MWCNT) has the highest total selectivity towards dihydroxyacetone and glyceric acid among tested ones (86 %).

2.3.3 Bimetallic Catalysts

Addition of Pt and Pd to Au catalysts was found to have a promoting effect in the various reactions of selective oxidation and was attributed to the synergetic effect due to alloy formation and is described in [68, 69]. The effect of bimetallic gold

catalysts on the product distribution in glycerol oxidation was also investigated. Addition of Pt and Pd was observed to improve catalyst activity and selectivity in glycerol oxidation. For example, a Au–Pd/C catalyst was shown to have higher selectivity to glyceric acid and higher activity than monometallic Au catalyst, the best results obtained under 300 kPa of oxygen, at 30–50 °C were 70–77 % selectivity to glyceric acid at 90 % conversion [70, 71]. The effect of preparation method of Au–Pt/C on the product distribution was studied in [72] at 300 kPa of oxygen, and 50 °C. The most active and selective catalyst for glyceric acid formation (62 % of selectivity) was prepared using H_2 as a reducing agent, while the other product was glycolic acid. The selectivity toward dihydroxyacetone at the expense to glyceric acid was improved from 26 % (Au/C) to 36 % (Au–Pt/C) by promoting the gold catalysts with platinum [75]. The advantage of using Au–Pd bimetallic catalysts is the catalyst stability, although some surface reconstruction and Pd leaching was observed [76]. Au–Pd catalyst has higher selectivity to glyceric acid, while it was less active [77]. Palladium was proposed to catalyze H_2O_2 decomposition formed on gold surface and hence the selectivity to glyceric acid was improved. In [74] the effect of the reaction parameters was studied using Au–Pd on activated carbon. The major products of glycerol oxidation were glyceric, glycolic and tartronic acids. It was revealed that selectivity to glyceric acid could be affected by applying different reaction conditions, thus, it increased from 52 to 80 % with: (i) decreasing of base loading (NaOH/glycerol ratio was 0.5 to 4 mol/mol); (ii) increasing substrate/metal ratio (was varied from 860 to 6900 mol/mol); (iii) increasing of oxygen pressure (from 1 to 6 bar). Catalytic activity was observed to be enhanced by loading of more catalyst and base.

2.3.4 Support Effect

The support effect on the catalyst performance was studied. The superior performance of Au/C compared to Au/TiO_2, Al_2O_3, MgO, CeO_2 in terms of activity and selectivity control was demonstrated by the group of Claus [67, 83]. Under the same experimental conditions the gold catalysts supported on carbon showed much higher activity in the liquid-phase oxidation of glycerol than magnesia and ceria supported gold catalysts [67]. Different carbon types were applied for gold catalyst preparation, and the effect of their pore structure on catalyst performance was investigated. Carbon pore structure was found to have a strong influence on Au/C catalyst activity, and in particular, supports with more micropores have demonstrated lower activity, although the product distribution was similar [75]. In [84], activity of Au/TiO_2 catalysts was thoroughly investigated. Catalysts were prepared by different methods, mainly deposition–precipitation (DP) and immobilization of gold sols. For the tested samples, gold particles were found to have two oxidation states (Au^0, $Au^{III/\delta+}$), while Au^0 was considered to provide the most active sites for oxidation of glycerol. The most active catalyst was found to be Au/TiO_2 prepared by DP, followed by chemical reduction using $NaBH_4$, while the

selectivity to glyceric acid was obtained over less active Au/TiO$_2$ (DP/calcined) catalyst. However, the turnover frequency (TOF) value of Au/C reported in their previous work [70] (1090 h^{-1}) was higher than TOF obtained for Au/TiO$_2$ catalyst prepared in similar way (178 h^{-1}) and the most active Au/TiO$_2$ (721 h^{-1}) (DP/NaBH$_4$), while the product distribution was similar in the studied cases. Thus, catalyst activity was demonstrated to be affected by the support.

Comparative catalytic studies of Au supported on Nb$_2$O$_5$, V$_2$O$_5$, Ta$_2$O$_5$, and Al$_2$O$_3$, TiO$_2$, C were performed [78]. Niobium oxide can reveal strong metal support interactions and is active in oxidation reactions [85]. Therefore, Au catalysts supported on group V metal oxides were tested in glycerol oxidation [78]. The reaction was conducted in the liquid-phase at NaOH/glycerol molar ratio equal to 2, at 60 and 90 °C, under 6 atm of oxygen. The main product of the reaction was glyceric acid in all studied cases. Results of this study have demonstrated that the highest conversion of glycerol was achieved over commercial Au/TiO$_2$, while among prepared catalysts, Au/Nb$_2$O$_5$ and Au/C demonstrated the highest glycerol conversion of 67 and 76 %, correspondingly. Moreover, the yield of glyceric acid was higher in case of niobium oxide supported gold.

Since Au/MgAl$_2$O$_4$ is a promising catalyst for gas-phase CO oxidation and liquid-phase ethanol oxidation to acetic acid [3, 4, 86], it was also investigated in liquid-phase glycerol oxidation. Selectivity was found to be correlated with the Al/Mg ratio in the support. An Al-rich surface gave the lowest C$_3$ product yield (glycerate and tartonate), while increasing of Mg fraction increased selectivity to C$_3$ products (60–70 %). Activity of the catalysts was influenced by amount of Au exposed. Therefore, catalytic behavior can be tuned by changing of spinel composition.

The relationship between carbon surface composition and Au/C catalyst performance in glycerol oxidation was studied in [87]. Carbon supports with different amounts of surface oxygenated groups were tested, while keeping their textural characteristics similar. The oxygen content on the surface had a strong influence on catalyst activity. A basic (oxygen-free) carbon support possesses a high density of π–electrons, which led to an increase in the reaction rate. However, the presence of surface functional groups did not affect the reaction selectivity. Total selectivity to glyceric acid and dihydroxyacetone was 80 %. Catalytic behavior of Au/C catalysts supported on multi-wall carbon nanotubes (CNT) and activated carbon (AC) was compared in [88]. Catalysts with similar metal loading and average Au particle size were found to have different selectivity to glyceric acid and gihydroxyacetone. A CNT-supported catalyst promoted dihydroxyacetone (60 %) formation due to preferential chemoselective orientation of glycerol for oxidation of secondary alcohol group. At the same conditions, reaction over Au/AC resulted mainly in formation of glyceric acid. More details of Au supported on multi-walled carbon nanotubes prepared by different methods evaluation were given in [82].

Gold catalysts supported on various carbonaceous materials were studied in the liquid-phase glycerol oxidation [89, 90]. Support structure affects the activity of Au particles, and then, activity and selectivity could be changed. In general, higher
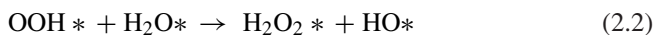
support crystallinity and smaller Au particle size, promote catalyst activity and selectivity. Similar results in terms of crystallinity were obtained in [78]. Higher activity of catalysts on supports with higher crystallinity in case of Au/C was associated with higher dispersion of Au particles.

Mesoporous carbon xerogels (CX) were considered to be promising catalyst supports for Au-catalyzed glycerol oxidation to gleceric acid, dihydroxyacetone, and glyceric acid [91]. The pore size of the support was found to have a strong influence on product selectivity. Wide pores are favorable for dihydroxyacetone formation, while narrow pores enhanced glyceric acid formation. Since pore size of CX can be easily modified, the reaction selectivity can be controlled.

Carbon-supported Au proved to be the best catalysts in glycerol oxidation due to such properties as acid and base resistance, porosity and controlled surface chemistry, and a possibility of metal recovery by combustion of the support [92, 93]. The approach to improve Au/C performance in glycerol oxidation is the synthesis of carbon materials with adjusted textural characteristics, surface chemistry and mechanical strength.

2.3.5 Kinetic Observations and the Reaction Mechanism

The effect of oxygen pressure was evaluated and glycerol oxidation rate was found to be independent of oxygen pressure in the range from 4 to 10 bar [67], 1 to 6 bar [74], 1 to 8 bar [90]. The mechanism of glycerol oxidation reaction is considered to be oxidative dehydrogenation as described in [94, 95]. Zope et al. [82] have studied liquid-phase glycerol oxidation by using labeled oxygen and water. This study indicated that during glycerol oxidation, glyceraldehyde ($HOCH_2CHOHCHO$) is the reaction intermediate produced by the initial dehydrogenation of the primary alcohol of glycerol. The base-catalyzed rapid interconversion of glyceraldehyde to dihydroxyacetone ($HOCH_2COCH_2OH$) during the oxidation reaction is involving more than two labeled oxygen atoms from water in the product. Molecular oxygen was found to play an indirect role during oxidation by forming hydrogen peroxide followed by hydroxide species formation. Oxygen activation follows formation and dissociation of hydrogen peroxide according to the reaction sequence:

$$O_2 * + H_2O* \rightarrow OOH * + HO* \tag{2.1}$$

$$OOH * + H_2O* \rightarrow H_2O_2 * + HO* \tag{2.2}$$

$$HO * + e^- \leftrightarrow HO^- + * \tag{2.3}$$

Moreover, the presence of adsorbed hydroxide species could lower the energy barrier for the C–H bond activation of alkoxide intermediate to form the aldehyde. The increasing of pH results in higher glycerol conversion and decreasing of activation energy to 5–12 kJ/mol [82, 90] compared to 50 kJ/mol [67] at lower pH.

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Chapter 3
Acetalization

Glycerol can be transformed to value-added chemicals via acetalization reaction. Glycerol formal (GF) is a mixture of two cyclic ethers: 5-hydroxy-1,3-dioxane and 4-hydroxymethyl-1,3-dioxolane (60:40) (Scheme 3.1). Acetalization of glycerol with formaldehyde can be catalyzed by homogeneous acids, such as H_2SO_4 [1, 2]. However, this approach leads to the reactor corrosion and waste of acid. An alternative way is to use a reusable catalyst for the required acidity .

In [3] heterogeneous Brønsted acid (zeolites and resins), Lewis acid (homogeneous catalyst based on gold salts), and a reusable gold complex were used in glycerol acetalization. The best result (94 % of yield) was achieved over a Lewis acid gold catalyst ($AuCl_3$). The reaction was performed at mild temperature (80–100 °C) using trioxane as a source of formaldehyde and dioxane as a solvent.
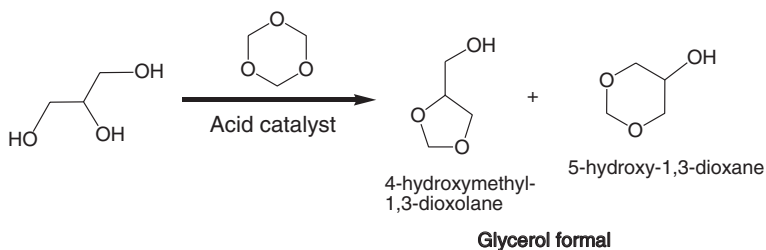
Scheme 3.1 Synthesis of glycerol formal (GF) using trioxane as source of formaldehyde. Reprinted from Ref. [3]. Copyright © 2010, with permission from Elsevier

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Chapter 4
N-Alkylation

Development of synthesis of fine chemicals and active pharmaceutical compounds requires improving of procedures for alcohol activation for nucleophilic substitution. In general, activation of alcohols can be performed by addition of either bases or acids. However, an alternative pathway involves oxidation of alcohols to corresponding ketones or aldehydes, which have wider reactivity than alcohols. Carbonyl compounds or their derivatives could be subsequently reacted to form various chemicals. The main reactions employing alcohol oxidation as an activation process are described in [1]: (a) condensation with amine, resulting in imine formation, and reduction to a different amine, (b) alkene formation and reduction to alkane, (c) enolization, electrophilic trap, and reduction to functionalized alcohol.

The redox steps of these reactions ("borrowing hydrogen") can be performed over catalysts effective in the reversible dehydrogenation of alcohols. There have been several attempts to apply gold catalysts well known for high selectivity in oxidation of alcohols [2] and hydrogenation of aldehydes, ketones, and imines [3]. Therefore, as a model reaction, alkylation of aniline by benzyl alcohol (Scheme 4.1) was studied over various gold catalysts (Au/TiO$_2$ [4–6], MgO [7], hydroxyapatite [8]). Gold-catalyzed alkylation of amines by alcohols under continuous operation mode was demonstrated in [9]. The reaction was performed under aerobic conditions, without addition of a base. In [10], the wide range of gold catalysts were tested in the *N*-alkylation of aniline with benzyl alcohol to produce a secondary amine. Selectivity to the secondary amine was found to depend on the type of support. Gold on ZrO$_2$ exhibited the highest catalytic performance and afforded 94 % selectivity to the secondary amine. This performance was attributed to surface hydroxyl groups on zirconia, which played important roles in the deprotonation of the alcohol in the alcohol dehydrogenation step, as the adsorption sites of aniline, and as the proton sources in the hydrogen transfer step.

Since certain alcohols can be derived from renewable feedstocks, this strategy can be considered as a biomass valorization approach. For example, the terpenes myrtenol and carveol, which are extracted from biomass, are widely used in the
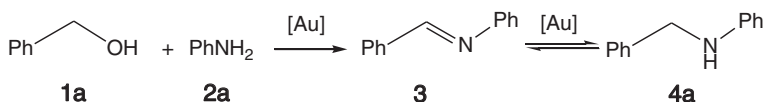
Scheme 4.1 Model reaction: alkylation of aniline by benzyl alcohol. Reproduced from Ref. [9] with permission of The Royal Society of Chemistry
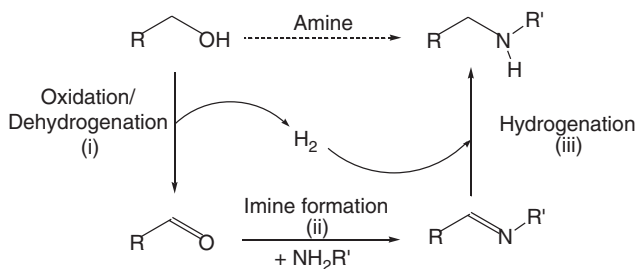
Scheme 4.2 Schematic view of the one-pot alcohols amination

development of new medicines. A prospective one-pot method for the production of complicated amines consists of three steps: (i) the dehydrogenation of alcohol to aldehyde, (ii) the condensation of aldehyde with primary amine to form imine via a hemiaminal intermediate, and (iii) the transfer of hydrogen to produce secondary amine (Scheme 4.2). In this reaction pathway, hydrogen generated by the step (i) can be used for step (iii), so that neither O_2 nor H_2 is required for the alcohol oxidation/dehydrogenation or hydrogenation of imine. In addition, water is the only by-product, similar to the *N*-alkylation of aniline with benzyl alcohol to produce secondary amine described in [10].
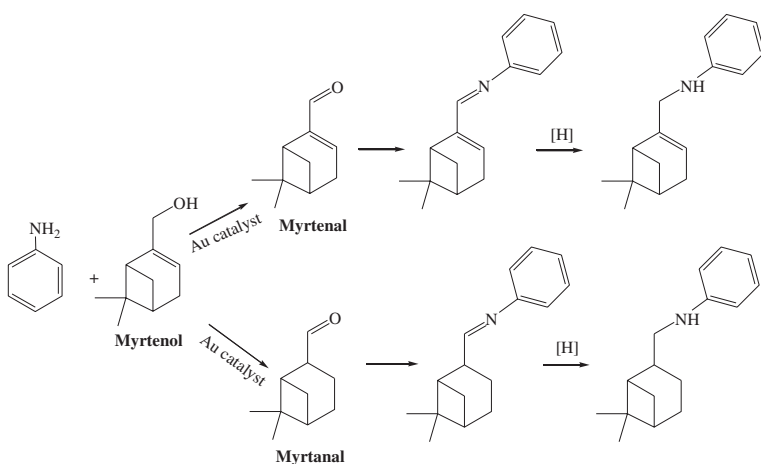
Scheme 4.3 Schematic view of the one-pot myrtenol amination by aniline

Amination of naturally occurring myrtenol and carveol with aniline to the corresponding amines over heterogeneous Au, Au–Pd, and Pd catalysts was studied in [11]. Myrtenol and carveol are used as model alcohol compounds with corresponding primary and secondary –OH groups (Scheme 4.3). The desired product is amine formed due to selective hydrogenation of imine, while keeping the double bond in the terpene structure. The selectivity of desired product depends on catalyst nanostructure, active component composition, and support. The activity and selectivity of the Au, Au–Pd, and Pd catalysts supported on ZrO_2, MgO, Al_2O_3, CeO_2, La_2O_3 were tested in the liquid phase at 500–900 kPa nitrogen pressure in temperature region 100–180 °C. The product distribution and conversion were shown to depend strongly on active metal component composition. Similar to results reported in [10], the most active and selective catalyst was found to be Au/ZrO_2. Zirconia supported catalyst that enables to transform myrtenol to unsaturated amines and imines at conversion of 95 % after 3 h at 180 °C and pressure of 900 kPa.

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Chapter 5
Selective Hydrogenation Reactions

The direct hydrogenation of aldehydes (such as maleic anhydride) over copper chromite can be performed efficiently [1]. However, because of the toxicity of chromium an alternative is desirable.

Selective hydrogenation of succinic anhydride (SAN) over gold catalysts was studied in [2]. Au/TiO$_2$ catalysts demonstrated higher activity (TOF of 104–158 mol$_{GBL}$ × h^{-1} × mol$_{Me}$$^{-1}$) than previously reported for Cu (TOF of 1.5 mol$_{GBL}$ × h^{-1} × mol$_{Me}$$^{-1}$) and noble metal catalysts (TOF of 1.5–153 mol$_{GBL}$ × h^{-1} × mol$_{Me}$$^{-1}$) in SAN hydrogenation, resulting in 97 % selectivity at 97 % conversion. Synthesis of GBL is the result of one carbonyl group hydrogenation, while further addition of hydrogen results in subsequent formation of BD and THF. Catalyst activity can be improved by using bimetallic Au–Pt/TiO$_2$ catalyst. Moreover, due to high selectivity toward GBL, it is possible to perform one-pot synthesis of pyrrolidone and pyrrolidone derivatives starting from GBL and ammonia or phenyl-amine (Scheme 5.1). The synthesis performed in water
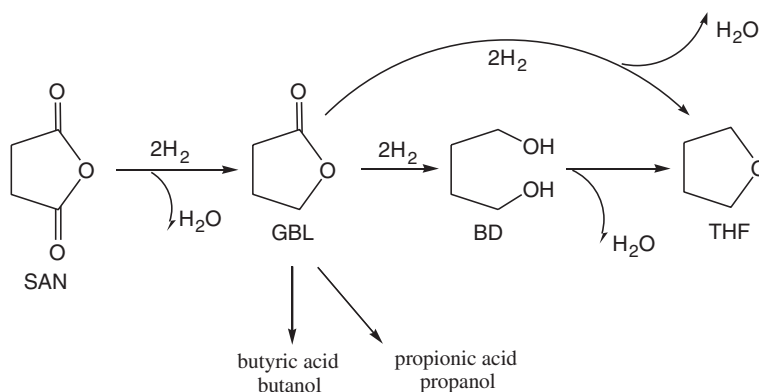
Scheme 5.1 The reaction pathway of hydrogenation and dehydration of succinic anhydride (SAN). Reprinted from Ref. [2], Copyright © 2008, with permission from Elsevier

under 120 bar, at 250 °C and substrate to gold molar ratio 700 mol/mol resulted in 80 % yield of pyrrolidones with 100 % selectivity for 10 h. The one-pot synthesis of phenylpyrrolidone was also performed with the yield of 52 %, while at extended reaction time phenylpyrrolidone was further hydrogenated to form phenylpyrrolidine.
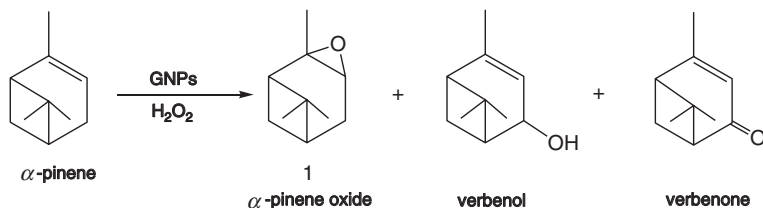
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Chapter 6
Double Bond Oxidation Reactions

Many homogeneous and heterogeneous catalysts were applied in the selective oxidation of α-pinene. A search for heterogeneous catalysts using green oxidants resulted in attempts to apply gold catalysts [1, 2]. In [1], oxidation of α-pinene was performed in the liquid phase at mild conditions (1 atm, 70 °C) and led to the formation of verbenol, verbenone, α-pinene oxide, and alkyl-pinene peroxide (Scheme 6.1). The effect of the solvent on catalyst activity was studied, and the highest conversion was demonstrated in the case when the substrate was dissolved in acetonitrile. The activity and selectivity of titania-supported Au, Cu, and bimetallic Au catalysts were also evaluated. The most active and selective catalyst toward verbenone formation among the tested materials was Au-Cu/TiO$_2$ catalyst prepared by deposition–precipitation with urea. The mechanism of the reaction described in [2] illustrates that alkoxy and alkyl-peroxy radicals were formed at the interface between the metal particles and the support via the adsorption of alkyl peroxide in the first step. In the second step, the produced radicals could react with α-pinene adsorbed on the metal surface, resulting in the formation of allyl and alkyl-pinene peroxy radical intermediates. In the final step, the products epoxide formed via the same pathway as well as verbenol and verbenone could be directly produced through by the decomposition of the intermediates and followed by the radical transformations.

Another reported study [1] was focused on α-pinene oxide synthesis, since campholenic aldehyde derived from rearrangement of α-pinene oxide is a valuable intermediate for manufacturing sandalwood-like fragrances [3, 4]. Gold supported on periodic mesoporous organosilicas, namely MCM-41, MSU, and SBA-15 ordered mesoporous silicas incorporated with bridging disulfide-ionic liquid moieties was applied in α-pinene oxide synthesis. Catalysts with the smallest Au particles (ca. 2 nm) exhibited the highest activity and selectivity to α-pinene oxide.

Scheme 6.1 Selective oxidation of α-pinene over gold nanoparticles (GNPs) in the presence of hydrogen peroxide. Reprinted from Ref. [1], Copyright © 2011, with permission from Elsevier

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Chapter 7
Isomerization Reactions

Despite that history of catalysis by gold started ca. 30 years ago, there are only few reports on isomerization reactions over supported gold. Some isomerizations include double bond migration in allylbenzene [1], skeletal rearrangements of propylene oxide to acetone [2], and cycloisomerization of γ-acetylinic carboxylic acids [3]. Among them there are two examples of biomass-derived compounds (linoleic acid and α-pinene) transformed by selective isomerization.
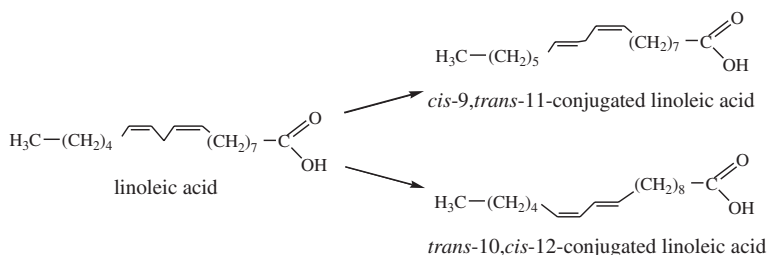
7.1 Isomerization of Linoleic Acid

An industrial method to synthesize conjugated linoleic acid (CLA) isomers comprises utilization of alkali metal and an organic solvent, which has drawbacks from ecological and economical point of view. These problems can be solved by utilizing heterogeneous catalysis. However, for successful reaction performance, preadsorption of hydrogen on the catalyst surface is needed. Thus, application of traditional catalysts (e.g., ruthenium) is a challenge due to hydrogenation of the unsaturated acid to produce saturated acid [4]. Nevertheless, utilization of ruthenium catalysts was found to be effective in [5], since no hydrogen pretreatment was needed.

Linoleic acid isomerization (Scheme 7.1) over gold catalysts on different supports was evaluated for the first time in [6]. The reaction was conducted at 150 °C, under a nitrogen flow. The desired isomers were obtained over gold on carbon with 100 % of selectivity.

7.2 Isomerization of α-Pinene

Industrial production of camphene starting from α-pinene is performed in the liquid phase at 150–170 °C over titania catalysts activated in situ by sulfuric acid [7]. The reaction rate is low and the yield of camphene is 35–50 %.

Scheme 7.1 Isomerization of linoleic acid to biologically active conjugated linoleic acid isomers (CLAs). Reprinted from Ref. [6], Copyright © 2008, with permission from Elsevier
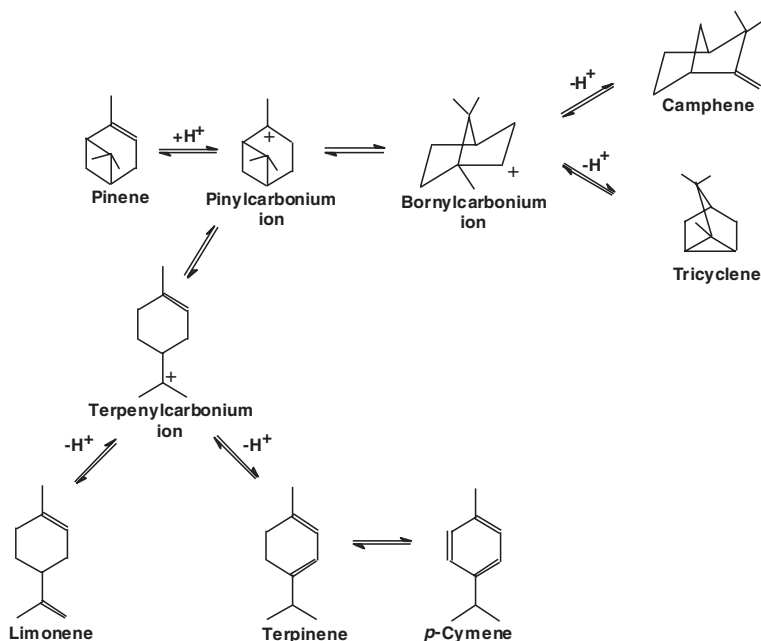
Scheme 7.2 Mechanism of α-pinene isomerization over acid catalysts. Reprinted from Ref. [8], Copyright © 2010, with permission from Elsevier

Camphene is formed from α-pinene via alkyl group migration to a neighboring carbon (Wagner-Meerwein rearrangement) (Scheme 7.2). For the first time, this reaction was performed over gold catalysts at 190–210 °C under continuous operation mode using a solution of the reagent in *n*-octane as the initial reaction mixture and hydrogen or nitrogen as a carrier gas in [8]. Utilization of 2.2 wt% Au/Al$_2$O$_3$ catalysts resulted in an increase of camphene yield up to 65 %, while the selectivity to camphene was 60–80 % at 100 % conversion of α-pinene. The reaction rate was found to be first-order with respect to α-pinene, and the rate constant was estimated to be 3–6 s^{-1}. High activity of gold in this reaction was hypothetically

attributed to the presence of cationic Au$^+$ species acting as Lewis acid sites, playing the key role in Wagner-Meerwein rearrangement. Moreover, it is possible to regenerate spent gold catalyst by treatment in an oxidative atmosphere.

Since this approach provides a possibility to perform the reaction over a solid reusable catalyst, thus avoiding the use of corrosive sulfuric acid while improving the camphene yield, it can be considered attractive from a practical point of view.

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Chapter 8
Gold Catalysts Stability

In general, long-term stability of catalysts is required for industrial applications. One of the most important advantages with respect to gold catalysts is their stability in oxidizing atmospheres. Catalyst deactivation can be caused, however, by other reasons, such as catalyst surface reconstruction, leaching of the active phase, strong adsorption of organic molecules and poisoning by inorganic compounds. Despite large efforts to explore catalysis by gold for many applications, reusability of gold catalysts and origin of deactivation were investigated for only a few reactions.

Long-term stability of gold catalysts in carbohydrate oxidation reactions was confirmed in [1–3, 5, 6, 13, 14]. However, carbon-supported gold catalysts used for glucose oxidation exhibited 50 % activity loss after 4 reaction runs primarily because of the severe leaching [14]. In contrast to carbon-supported catalysts, gold supported on metal oxides has excellent performance in carbohydrate oxidation. Thus, Au/TiO_2 has demonstrated no activity loss after 17 runs in the same reaction in [5]. Likewise, no activity (or selectivity) decrease in glucose oxidation over Au/Al_2O_3 was observed after 10 runs [5]. Continuous-flow liquid-phase oxidation of glucose was for the first time shown in [13], confirming that alumina-supported gold catalysts did not have any loss of activity and selectivity for 70 days. Gold-catalyzed glucose oxidation is therefore a promising alternative to the existing industrial approach based on a biotechnological process involving extensive separation/purification steps. Robustness of supported gold catalysts in the selective oxidation of other carbohydrates, such as maltose, lactose, arabinose and galactose, was also observed [1–3], while the reaction was performed for 3 h.

Selective oxidation of alcohols and polyalcohols over gold catalysts was investigated extensively, although details about catalyst stability are often omitted. In gas-phase ethanol oxidation under continuous operation, deactivation of gold catalysts was observed at temperatures below 220 °C. Ethanol conversion decreased from 50 % to 30 % within 1 h, while the activity was completely restored by calcination in an oxygen atmosphere at 400 °C [4]. Carbon-supported gold catalysts were shown to be more active and selective in glycerol oxidation compared to metal oxide supported catalysts at the same reaction conditions [9, 10]. A slight decrease of Au/C, Nb_2O_5 activity in glycerol selective oxidation was reported

in [8, 11]. Gold catalysts demonstrated long-term stability in glycerol oxidation performed in a continuous fixed-bed reactor [15], with a Au/TiO_2 catalyst operating more than 50 h on stream. However, inhibition of the catalyst activity was attributed to the strong adsorption of ketone intermediates and products of ketone condensation in [16], which could be found in biomass-derived feedstocks. It is important to note that the data obtained in the laboratory tests are not sufficient yet for scaling up the catalysts and the process to an industrial application level.

Reusability of gold catalysts in α-pinene isomerization was investigated in [12]. The deactivated catalyst contained the carbonaceous deposits that may block the catalyst surface. Calcination in oxygen flow at 650 °C to eliminate coke deposits resulted in almost complete catalyst regeneration (see Fig. 8.1). Moreover, no gold particles sintering during catalyst regeneration procedure was observed. Further investigation of gold catalyst (2.2 wt. % Au/Al_2O_3) stability in α-pinene isomerization revealed the dependence of catalyst deactivation on the inlet concentration of the substrate varied in the range of 0.4 – 20 vol. %. In particular, the catalyst deactivation was negligible at α-pinene inlet concentration of 0.4 vol. %, and no selectivity decline towards camphene (65 %) with time-on-stream was observed [17].

For other reactions, deactivation could be much more prominent. For example, gold catalysts deactivated in the selective oxidation of the lignan HMR [7]. Consecutive reaction runs with addition of the fresh catalyst (Fig. 8.2) clearly demonstrated the increase of the catalyst activity after such addition, which suggested that decline of activity could be due to presence of strongly adsorbed product and impurities in the substrate. Other factors, such as catalyst leaching and gold particle agglomeration, could also explain the decline in catalyst activity, while their impact was minor. Calcination in an oxidizing atmosphere was the most successful approach for regeneration, although the activity was still rather low due to incomplete combustion of the organic compounds on the catalyst surface. The regeneration procedure by combustion of organic deposits is, however, challenging due to the possibility of sintering Au particles at high temperature and thus decreasing the availability of surface gold atoms for catalysis.

Fig. 8.1 Time dependence of α-pinene conversion and selectivity to camphene over the 2.2 % Au/Al_2O_3 catalyst taken as-prepared and after regeneration in flowing O_2 at 60–650 °C. Reprinted from [12], Copyright © 2010, with permission from Elsevier
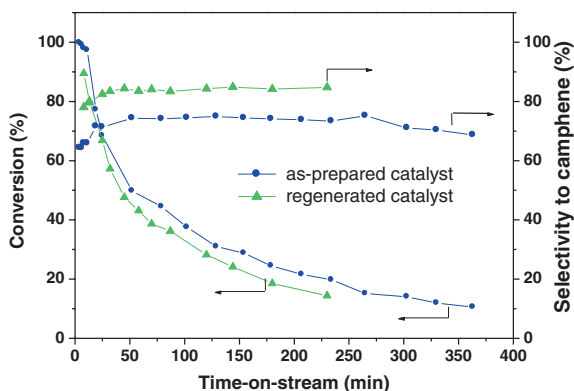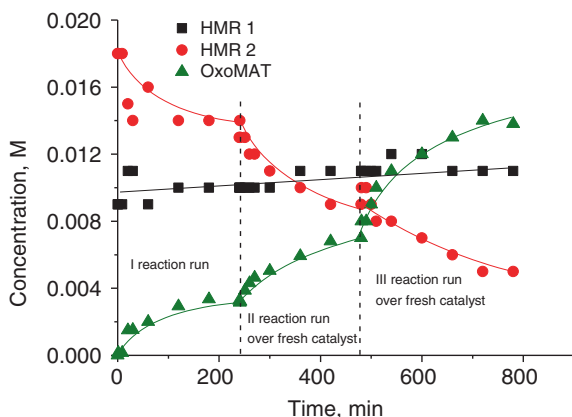
Fig. 8.2 Consequent selective oxidation of the lignan HMR with fresh catalyst 2 wt % Au/Al$_2$O$_3$, 70 °C. Reprinted from [7] (Figure 3, Copyright © 2012, Springer Science + Business Media, LLC). With kind permission from Springer Science and Business Media

Although the long-term stability of gold catalysts is an important issue, it should be emphasized that it has not been studied thoroughly. The few examples available in the literature do not provide a consistent picture of deactivation. Excellent stability of gold catalysts in carbohydrate oxidation reactions makes gold a potential catalyst for industrial application. However, in some cases, the regeneration of gold catalysts is challenging and more efforts are needed to make an industrial process feasible.

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Chapter 9
Summary

Growing interest for biomass valorization approaches in the recent years has led to an increase of research related to the application of gold catalysts in the transformation of biomass-derived compounds. Gold catalysts have demonstrated outstanding performance in a number of reactions. Applications of gold as a catalyst have several advantages such as stability under oxidative atmosphere, high selectivity toward products of partial oxidation and hydrogenation, as well as acetalization and isomerization. Moreover, gold catalysts allow operation at mild and therefore environmentally friendly conditions, using molecular oxygen as an oxidant, lower pressure and temperatures, and in some cases water as a solvent. More efforts should be however devoted to elucidating long-term stability of gold catalysts and in case of deactivation, development of efficient catalyst regeneration methods. Due to a synergetic effect, bimetallic gold catalysts in some cases have higher activity. Thus, addition of such metals, as copper could increase the process profitability.

While valorization of the most abundant feedstocks such as glycerol, carbohydrates and their derivatives was studied extensively, other processes still needed to be developed. Synthesis of fine chemicals from biomass extractives is one of the developing fields for catalysis by gold. Unique properties of gold as a catalyst are under intensive investigation, which will result in growing application of these catalysts in a variety of reactions in general, and in particular, in biomass-derived compounds transformations.

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