SELECTIVE OXIDATION OF ALCOHOLS AND ALDEHYDES WITH GOLD NANOPARTICLE CATALYSTS

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ACADEMIC DISSERTATION

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Abstract

Selective catalytic transformations are essential for the sustainable production of chemicals using renewable biomass feedstocks. In particular, catalytic oxidations utilizing oxygen or hydrogen peroxide reduce the use of toxic chemicals providing environmentally benign routes to replace petroleum-derived chemicals. Recently, catalysts based on gold nanoparticles have gained a lot of interest due to their excellent performance, stability and reusability in selective oxidation under mild conditions, and especially in oxidation of biomass-derived substrates.

In this thesis, selective and environmentally friendly methods for oxidation of alcohols, aldehydes and carbohydrates were developed using gold nanoparticles supported on metal oxides. The work expands the substrate scope of gold catalysts and, on the other hand, elucidates the effect of reaction conditions on the oxidation.

The effect of reaction media on the chemoselectivity of gold catalysis was studied using benzyl alcohol as a model compound. As a result, we introduced a new “one for all” concept for oxidation of alcohol into a variety of products. In a further study, vanillic acid was produced by oxidation of vanillin, an aromatic aldehyde available from biomass lignin.

Oxidation of carbohydrates with gold catalysts was studied both in alkaline and base-free conditions. Uronic acids, available from hemicelluloses and pectin, were selectively oxidized into sugar diacids under very mild conditions. Base-free oxidation of glucose to gluconic acid was studied using microwave irradiation and hydrogen peroxide as green oxidant. In both studies, significantly shortened reaction times and very high activities compared to previous reports were achieved.

Preface

I want to express my gratitude to my supervisors Prof. Timo Repo and Prof. Markku Leskelä, without whom this work would not have been possible. I am most thankful for the opportunity to explore the field of heterogeneous catalysis and for all the support you have provided. Timo, I owe you my deepest gratitude for the countless discussions, encouragement and guidance you have offered me during these years.

I am truly grateful to the all co-authors for their help and contribution to this work. I am most indebted to Prof. Dmitry Murzin from Åbo Akademi for the successful collaboration and valuable support especially at the start of this work. I also want to thank his former group members, particularly Dr. Olga Simakova, for their hospitality and help. I owe my thanks to Dr. Klaus Niemelä from VTT for his valuable contribution and for showing true interest in this work.

I sincerely appreciate Dr. Marko Vehkamäki, Dr. Marianna Kemell and Mikko Heikkilä for sharing their knowledge and for their invaluable work on catalyst characterization. I have also had the pleasure to work with highly talented students, Jingjing Chen and Petra Lehtinen, and I want to thank you for assisting with the research.

I owe my thanks to all of my co-workers at Catlab for their support and friendship and for making Catlab such an enjoyable place to work. I am especially grateful to Tiina, Markus, Pauli, Maija, Sirpa, Emi and Jesus; thank you for your continuous friendship also outside the lab.

I am deeply thankful to my parents for their constant love and care, and for encouraging me to find my own path. This thesis would not exist without your endless support.

Mikko, your love, patience and understanding has been vital to me. Words are not enough to express my love for you.

Helsinki, March 2016

Sari Rautiainen

List of original publications

This thesis is based on the following publications:

I Sari Rautiainen, Olga Simakova, Hongfan Guo, Anne-Riikka Leino, Krisztián Kordás, Dmitry Murzin, Markku Leskelä and Timo Repo: Solvent controlled catalysis: Synthesis of aldehyde, acid or ester by selective oxidation of benzyl alcohol with gold nanoparticles on alumina. *Appl. Catal. A* **2014,** 485, 202-206.

II Sari Rautiainen, Petra Lehtinen, Jingjing Chen, Marko Vehkamäki, Klaus Niemelä, Markku Leskelä and Timo Repo: Selective oxidation of uronic acids into aldaric acids over gold catalyst. *RSC Adv.* **2015**, 5, 19502-19507.

III Sari Rautiainen, Petra Lehtinen, Marko Vehkamäki, Klaus Niemelä, Marianna Kemell, Mikko Heikkilä and Timo Repo: Microwave-assisted base-free oxidation of glucose on gold nanoparticle catalysts. *Catal. Commun.* **2016**, 74, 115-118.

IV Sari Rautiainen, Jingjing Chen, Marko Vehkamäki and Timo Repo: Oxidation of vanillin with supported gold nanoparticles. *Top. Catal.* accepted

The publications are referred to in the text by their roman numerals.

List of other publications

V Hongfan Guo, Marianna Kemell, Afnan Al-Hunaiti, Sari Rautiainen, Markku Leskelä and Timo Repo: Gold-palladium supported on porous steel fiber matrix: Structured catalyst for benzyl alcohol oxidation and benzyl amine oxidation. *Catal. Commun.* **2011,** 12, 1260-1264.

VI Hongfan Guo, Afnan Al-Hunaiti, Marianna Kemell, Sari Rautiainen, Markku Leskelä and Timo Repo: Gold Catalysis Outside Nanoscale: Bulk Gold Catalyzes the Aerobic Oxidation of π-Activated Alcohols. *ChemCatChem* **2011,** 3, 1872-1875.

Author's contribution

In paper I, the author performed the oxidation experiments and drafted the manuscript. Olga Simakova prepared the Au catalyst under supervision of Prof. Dmitry Murzin. Dr. Hongfan Guo assisted with the research. Anne-Riikka Leino and Dr. Krisztián Kordás performed TEM analysis. The work was done under supervision of Prof. Markku Leskelä and Prof. Timo Repo. All authors took part in preliminary revision of the paper.

In paper II, the author performed the experiments with the help of Petra Lehtinen and Jingjing Chen. The author prepared and characterized the Au catalyst except for TEM analyses which were carried out by Dr. Marko Vehkamäki. Dr. Klaus Niemelä performed GC/MS analyses. The work was done under supervision of Prof. Markku Leskelä and Prof. Timo Repo. The author drafted the manuscript, and the final version was discussed and approved by all authors.

In paper III, the author performed the experiments and prepared the catalysts with the help of Petra Lehtinen. TEM analyses were done by Dr. Marko Vehkamäki. Dr. Klaus Niemelä performed GC/MS analyses. Dr. Marianna Kemell and Mikko Heikkilä carried out SEM and XRD measurement, respectively. The work was done under supervision of Prof. Timo Repo. The author drafted the manuscript, and the final version was modified and approved by all authors.

In paper IV, the author performed the experiments and prepared the catalysts. Jingjing Chen performed preliminary experiments. TEM analyses were done by Dr. Marko Vehkamäki. The work was done under supervision of Prof. Timo Repo. The author drafted the manuscript, and the final version was modified and approved by all authors.

Abbreviations

AAS	atomic absorption spectrophotometer
AC	activated carbon
BA	benzyl alcohol
CNF	carbon nanofibre
CNT	carbon nanotube
DIE	direct ion-exchange
DPU	deposition-precipitation with urea
EDS	energy dispersive spectrometer
FDCA	2,5-furandicarboxylic acid
FESEM	field emission scanning electron microscopy
Gly	glycerol
HFCA	5-hydroxymethyl-2-furancarboxylic acid
HMF	5-hydroxymethylfurfural
HT	hydrotalcite
MOF	metal-organic framework
NMR	nuclear magnetic resonance
PVA	polyvinyl alcohol
PVP	poly(*N*-vinyl-2-pyrrolidone)
RT	room temperature
SEM	scanning electron microscopy
STEM	scanning transmission electron microscopy
TEM	transmission electron microscopy
TGA	thermogravimetric analysis
TOF	turn-over frequency
TON	turn-over number
XRD	X-ray diffraction

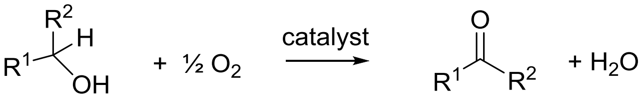
Table of contents

1 Introduction

Gold has fascinated human for thousands of years due to its unique qualities, lustrous appearance, high stability and great malleability. Bulk gold is very inert and resistant to oxidation due to its high electrode potential ($E^0 =$ +1.691 V), and therefore it was long thought that gold is chemically inactive. When dispersed as very small nanoparticles however, gold has some emergent properties. For instance, the surprising ruby red colour of gold nanoparticles has been employed in glassmaking since ancient times. During the last decades with the advent of nanotechnology, scientists in various fields have found interest in gold nanoparticles.[1] In the 1980s, Haruta and co-workers found that gold nanoparticles supported on metal oxides are extremely active catalysts for oxidation of carbon monoxide at temperatures much lower than the traditionally used palladium or platinum.[2] Another ground-breaking discovery was made by Hutchings, who showed gold as the best catalyst for acetylene hydrochlorination.[3] These findings incited a new "gold rush" in science and the application of gold in catalysis is growing rapidly.[1,4]

By definition, a catalyst increases the rate of a chemical reaction by decreasing energies of the transition states, but it is not consumed itself in the process. Catalysis occurs very widely both in nature and industrially, being vital to all living organisms and also extremely important in today's society. Gold nanoparticles deposited on a solid support are considered to be a heterogeneous catalyst, as the reactants are in gas or liquid phase while the catalyst is solid. The catalytic reaction requires adsorption of the reactants on the metal surface, and consequently decreasing the size of the particles increases the surface area available for the reaction. In particles around 2 nm in diameter, more than half of the gold atoms are on the surface of the particle.[5] The surface atoms have low coordination number which makes them reactive, and this also affects physical properties of the particle, such as melting point and conductivity. It is worth mentioning that in parallel with the development of gold nanoparticle catalysts, homogeneous gold catalysis has progressed tremendously.[6] This is however beyond the scope of this thesis, and therefore the term *gold catalyst* refers to heterogeneous gold nanoparticle catalysts herein.

Selective oxidation is a fundamental transformation in chemistry and also of great industrial importance. Conventionally, oxidation reactions are carried out using strong stoichiometric oxidants, such as chromates, which are expensive and produce large amounts of toxic waste. Therefore, there is considerable need for more beneficial and sustainable technologies. Catalytic oxidation employing oxygen or hydrogen peroxide as terminal oxidant is a very atom-efficient method, as water is the only by-product (Scheme 1).[7,8] Transition metals including Pd, Pt and Ru have been extensively studied, both as homogeneous and heterogeneous catalysts, for selective oxidation.[9] In a benchmark study by Mori *et al.*, palladium nanoclusters supported on hydroxyapatite showed very high activities up to 10000 h^{-1} in aerobic oxidation of aromatic alcohols.[10] While heterogeneous catalysts have often suffered from low selectivities, the Pd catalyst produced over 90% of the corresponding aldehyde.



Scheme 1 General scheme for aerobic oxidation of alcohols.

Traditionally, selective oxidation reactions have been associated with the functionalization of petroleum-based feedstocks to oxygenated compounds such as alcohols, carbonyl compounds and epoxides. However, the sustainable production of chemicals and fuels requires renewable feedstocks, *e.g.* biomass, as replacements for fossil resources.[11] Biomass is chemically very different compared to crude oil, as it is already highly functionalized by oxygen. Therefore, a great deal of research is needed to develop efficient and environmentally-friendly methods for biomass conversion in biorefineries.[12,13] Especially, heterogeneous noble metal catalysts have received an increasing amount of attention in biomass processing.[14] The major advantage of heterogeneous catalysts is their easy separation from the reaction mixture, allowing recycling of the catalyst and reducing the amount of waste produced.

Selective oxidation of biobased compounds, such as polyols and carbohydrates, produces fine chemicals which have applications within the food, pharmaceutical, cosmetic and polymer industries.[15,16] However, these are challenging substrates for oxidation, as they contain multiple functional groups, and therefore the selectivity of the reaction warrants particular consideration. In this respect, catalysts based on gold nanoparticles have shown excellent performance, stability and reusability in oxidation of alcohols and sugars under mild conditions, surpassing catalysts based on other metals, such as Pd and Pt.[15]

2 Scope of the thesis

The aim of this work was to develop efficient and environmentally friendly methods for oxidation of alcohols and aldehydes using gold nanoparticle catalysts, with special emphasis on biomass-derived substrates. Accordingly, the literature review of this thesis focuses on oxidation of some the most important biomass-derived compounds, such as glycerol, 5-hydroxymethylfurfural and carbohydrates, outlining the milestones achieved and relevant progress in catalyst development. In addition, the oxidation of benzyl alcohol is examined as a model reaction for selective oxidation.

This thesis is based on four original publications (attached at the end of the thesis), which are referred to as I-IV. The motivation and the most important findings of each paper are discussed in the Results and discussion section (p. 32). Based on the substrates, the work can be divided in the oxidation of aromatic alcohols and aldehydes,[I,IV] and oxidation of carbohydrates.[II,III]

In the first part of this study, the effect of reaction conditions on the selectivity of benzyl alcohol oxidation was studied. The objective was to achieve control over the product distribution by changing the reaction conditions. The study inspired the author to investigate the oxidation of vanillin, an aromatic aldehyde available from lignin, for the first time with gold catalysts.

The oxidation of carbohydrates was studied both in alkaline and base-free conditions. During the studies, method for the selective oxidation of uronic acids into the corresponding aldaric acids was developed. In addition, a novel efficient method for base-free oxidation of glucose was introduced.

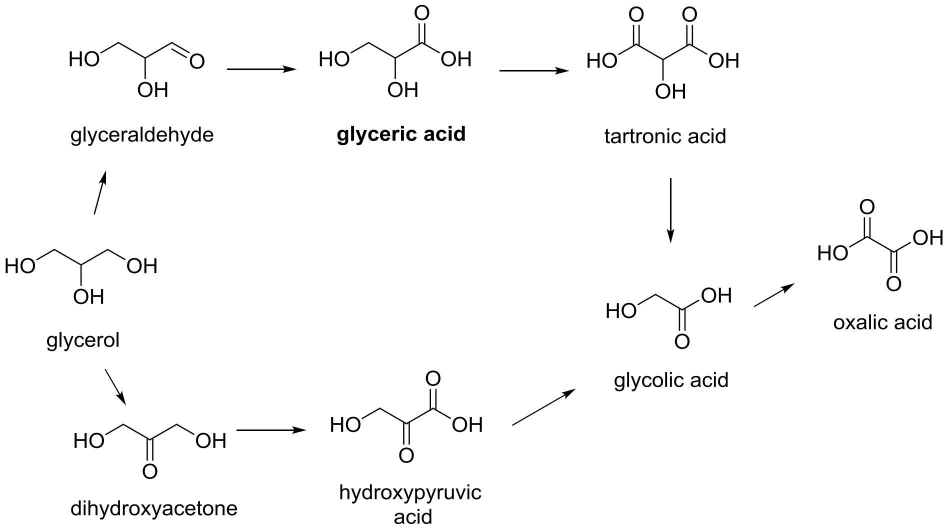
3 Literature review

3.1 Oxidation of alcohols

In the late 1990's, Prati and Rossi reported the first alcohol oxidations using gold nanoparticles supported on carbon and alumina.[17] Ethane-1,2-diol (ethylene glycol) and propane-1,2-diol were oxidized into the corresponding monoacids with high selectivities in alkaline aqueous solution. The study gave the first examples of the peculiar chemoselectivity of gold catalysts in comparison with conventional palladium and platinum-based oxidation catalysts. First, gold showed higher selectivity towards monooxidation of ethane-1,2-diol to glycolate whereas with Pd and Pt catalysts, overoxidation of glycolate to oxalate decreased selectivity. Second, in the case of propane-1,2-diol, gold favoured the oxidation of the primary hydroxyl group over the secondary, giving total selectivity to lactate. Moreover, gold catalysts showed higher stability in recycling experiments compared to Pd and Pt catalysts.

3.1.1 Oxidation of glycerol

Glycerol is a renewable chemical available in large quantities from production of biodiesel by transesterification of triglycerides. The oxidation of glycerol can yield several valuable products *via* a complex reaction pathway, and therefore control over the selectivity presents a major challenge (Scheme 2). Hutchings' group extended the study of gold catalysis to oxidation of glycerol; 100% selectivity to glyceric acid at 56% conversion was achieved using Au/C (Table 1, entry 1).[18] The reaction conditions were rather mild, but addition of sodium hydroxide was necessary to obtain any conversion. Under similar conditions, Pd/C and Pt/C gave ca. 65% selectivities, though both were active to some extent also in acidic conditions.[19] Owing to the industrial interest as well as the exceptional selectivities, glycerol is one of the most studied substrates in gold-catalysed oxidations.[20] Selected results are presented in Table 1.



Scheme 2 Possible products of glycerol oxidation. Adapted from refs.[21,22]

Table 1 Oxidation of glycerol to glycerate in alkaline aqueous solution with gold catalysts.

Entry	Catalyst	Gly: Au	NaOH (equiv.)	Conditions	Conv. (%)	Sel. (%)	Ref.
1	Au/C	538	1	3 bar O_2, 60 °C, 3 h	56	100	[18]
2	Au/C	3500	2	10 bar O_2, 60 °C, 3 h	100	75[a]	[23]
3	Au/C	8000	2	11 bar O_2, 60 °C, 0.5 h	7	67	[24]
4	Au/TiO_2	8000	2	11 bar O_2, 60 °C, 0.5 h	33	64	[24]
5	Au/TiO_2	8000	2	10 bar O_2, 60 °C	78	70	[25]
6	Au/NiO-TiO_2	1000	4	3 bar O_2, 50 °C	90	75	[26]
7	Au/$MgAl_2O_4$	1000	4	3 bar O_2, 50 °C	50	63	[27]

[a] Selectivity reported at 30% conversion.

Under alkaline conditions, glyceric acid, or glycerate, is usually the main product with gold catalysts. However, several factors affect the selectivity, such as the amount of base, oxidant, gold particle size and the catalyst support. Using Au/C, the optimal activity and selectivity to glyceric acid were obtained with 2 equiv. of NaOH (Table 1, entry 2).[23] With 4 equiv., subsequent oxidation of the monoacid to tartronic acid was favoured. Even though the diacid is an interesting product, the highest reported tartronic acid yield is only 45% over a Au/TiO_2 catalyst.[21] The difficulty of the subsequent oxidation to diacid was explained by catalyst inhibition due to adsorption of ketone intermediates or condensation products.[28]

The C–C bond cleavage produces glycolic acid and other C_2 and C_1 products. Interestingly, the selectivity to glycolate increases with decreasing Au particle size.[23,29] Optimal average particle size of Au/C was 3.7 nm for high glyceric acid selectivity (75%), whereas 2.7 nm particles gave only 40% glyceric acid. The smaller particles are more active in producing hydrogen peroxide, which in turn is responsible for the C–C cleavage. As glycolic acid is also a valuable product, Sankar *et al.* utilized this reaction to produce glycolate directly by oxidation of glycerol with H_2O_2.[21]

Gold catalysts supported on various carbonaceous materials are the most studied and so far the most active catalysts in glycerol oxidation.[16] The highest turn-over frequencies up to 60 000 h^{-1} were obtained with Au/C catalysts.[30] The surface chemistry of the carbon support has an important role in determining the properties of the catalyst.[31] For instance, carbon nanotubes containing basic functionalities showed increased activity, whereas hydrophobicity of the carbon surface increased selectivity towards C_3 products.[32] Moreover, the support structure can also affect the morphology and orientation of Au particles on carbon nanofibres.[33] On a more ordered graphitic surface, Au particles oriented their (111) planes parallel to the nanofibres which increased H_2O_2 production and consequently the amount of C_2 and C_1 products (77%). On a disordered carbon surface Au NPs were randomly oriented and 56% selectivity to C_3 products was achieved.

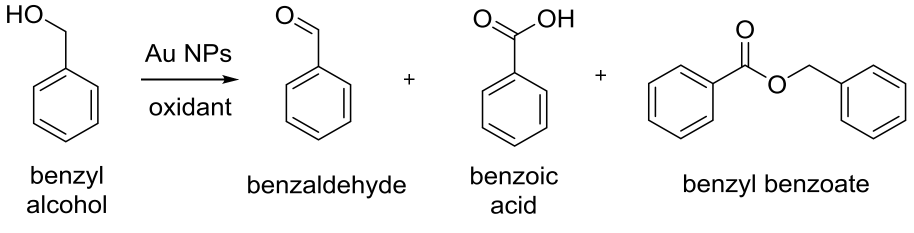
Metal oxide supported gold catalysts have also been effective in glycerol oxidation, and Au/TiO_2 catalysts are among the most investigated. According to Zope *et al.*, Au/C and Au/TiO_2 gave similar selectivities, while Au/C showed slightly higher initial activity despite the three times larger particles (Table 1, entries 3 and 4).[24] Similar results were obtained by Davis's group, though in this case the initial activities with Au/C were four times greater than with Au/TiO_2 (entry 5).[25] In a study by Prati's group, the activity of Au/TiO_2 increased when NiO was mixed with the titania support.[26] Compared to pure Au/NiO, selectivity of Au supported on NiO-

TiO_2 mixed oxides was significantly higher (entry 6). Catalyst characterization revealed preferential deposition of Au particles on NiO, changing the interactions between Au and the support.

Prati's group also studied the effect of support structure with Au/$MgAl_2O_4$ catalysts.[27] Preparation method of the $MgAl_2O_4$ spinel supports and consequently their surface properties had a significant effect on selectivity. The highest selectivity to glycerate (63%) was observed when Mg was enriched on the support surface (entry 7), whereas Al-rich surface led to low selectivity (25%). However, activity of the spinel catalysts was influenced mainly by the amount of exposed gold.

3.1.2 Oxidation of benzylic alcohols

Benzyl alcohol (BA) is one of the most studied substrates in oxidation of alcohols and it has also been thoroughly investigated in gold catalysis. The reactivity of benzyl alcohol is very high due to the activation of the aromatic ring.[16] While benzaldehyde is the most common product, the oxidation is sensitive to changes in reaction conditions, and consequently benzoic acid[34] and benzyl benzoate[35] have also been reported as main products (Scheme 3). In addition to BA, a number of other benzylic and aromatic alcohols have been oxidized with gold catalysts.



Scheme 3 Possible products of benzyl alcohol oxidation by gold catalysts.

Polyvinylpyrrolidone-stabilized gold nanoparticles (Au:PVP) oxidized benzyl alcohol into benzoic acid in alkaline water at ambient conditions (Table 2, entry 1).[34,36] Polymer-stabilized nanoparticles can be considered the borderline between homogeneous and heterogeneous catalysis. The Au particles are only weakly stabilized by the polymer which allows one to study the inherent properties of the particles without the effect of the support. Comparison of Au particles with different particle sizes showed that the activity, when calculated according to the exposed Au surface area, clearly depends on the particle size. The rate constant of the small particles (1.3 nm) was three orders of magnitude higher than the large ones (9.5 nm).[34] Moreover, the small Au particles were at least one order of magnitude more active than Pd particles under similar conditions.

Our group also showed that bulk gold can oxidize alcohols, contrary to common belief, though the system was sensitive towards both substrate structure and solvent.[VI] Only aromatic alcohols, such as BA and cinnamyl alcohol were oxidized, indicating that π-activation by the phenyl ring is necessary to facilitate the reaction. Surprisingly, heptane was the best solvent for the oxidation, and only BA was oxidized in toluene.

Table 2 Oxidation of benzyl alcohol into benzaldehyde with gold catalysts.

Entry	Catalyst	BA:Au	Solvent	Conditions	Conv. (%)	Sel. (%)[a]	Ref.
1	Au:PVP	50	water	3 equiv. K_2CO_3, air, 27 °C, 6 h	100	85[b]	34
2	Au/steel fibre	5700	water	1 equiv. NaOH, 5 bar O_2, 80 °C, 3 h	75	90[b]	V
3	Au/Al_2O_3	900	-	1.5 bar O_2, 130 °C, 5 h	69	65	37
4	Au/C	76000	-	10 bar O_2, 160 °C, 6 h	48	64	38
5	Au/TiO_2	76000	-	10 bar O_2, 160 °C, 6 h	67	64	38
6	$Au/Ga_3Al_3O_9$	200	-	O_2 flow, 80 °C, 2 h	98	>99	39
7	Au/TiO_2	1000	biphasic[c]	10 bar O_2, 100 °C, 8 h	83	93	35
8	Au/HT[d]	240	*p*-xylene	no oxidant, 120 °C, 6 h	>99	>99	40
9	Au/NaY[e]	110	toluene	1 equiv. K_2CO_3, air, 80 °C, 5 h	>95	>99	41
10	Au/MIL-101[f]	100	toluene	O_2 flow, 80 °C, 1 h	>99	>99	42

[a] Selectivity to benzaldehyde unless otherwise stated. [b] Selectivity to benzoic acid. [c] Water:*p*-xylene = 7:1 (mol:mol). [d] Gold on hydrotalcite. [e] Gold on zeolite Y. [f] Gold on metal-organic framework.

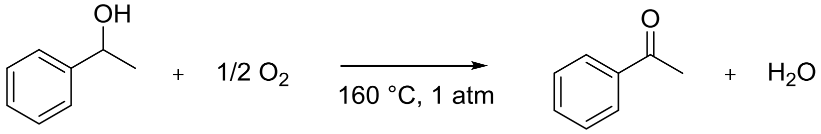
A simple and clean preparation method for gold catalyst supported on porous steel fibre matrix was developed in our group.[V] Using sputtering method, the fibre was coated with a thin gold film, with nominal thicknesses from 0.5 nm to 6 nm. The porous structure of the fibre matrix gives the material high surface area. Without any further treatment, the fibre matrices oxidized BA into benzoic acid in alkaline aqueous solution with activities close to 4000 h^{-1} (entry 2).

Even though water is a safe and environmentally friendly solvent, the solubility of substrates limits its use. Solvent-free transformations, when feasible, can be considered an even greener alternative. Choudhary *et al.* studied the oxidation of benzyl alcohol without additional solvent or base using several metal oxide supported catalysts.[37] The solvent-free oxidation produced benzaldehyde with small amounts of benzyl benzoate as side product. Gold supported on alumina was one of the most active and also had the smallest particle size among the studied catalysts (entry 3). Zheng *et al.* demonstrated that the addition of a small amount of base promotes the solvent-free oxidation of BA.[43] The activity of Au/TiO_2 catalyst increased from 19 h^{-1} to 7800 h^{-1} with addition of only 0.2 mol% K_2CO_3, though a decrease in selectivity was observed.

Hutchings' group compared gold supported on titania and carbon prepared by sol immobilization using polyvinyl alcohol (PVA) as a protecting agent.[38] The catalysts displayed narrow particle size distributions and gave very high activities in BA oxidation even without added solvent or base (entries 4 and 5). TOF values over 30000 h^{-1} were measured with Au/TiO_2 which was calcined in air prior to the oxidation to remove PVA residues. However, the catalyst surface was modified by the calcination treatment leading to decreased benzaldehyde selectivity and formation of benzoic acid and toluene as side products with 20% selectivities.

A very active catalyst for solvent-free alcohol oxidation was developed by supporting gold on nanosized cerium oxide.[44] The catalyst oxidized 1-phenylethanol into acetophenone with 99% selectivity at atmospheric oxygen pressure, giving the highest TOF value (12500 h^{-1}) reported for the reaction at that time (Scheme 4). The nanocrystalline ceria support was able to oxidize alcohols stoichiometrically on Lewis acidic Ce^{3+} centres, but gold was needed to complete the catalytic cycle. Similar behaviour was not observed with conventional microcrystalline CeO_2. Even higher activities in

1-phenylethanol oxidation were achieved with gold supported on Ga-Al mixed oxides, Au/$Ga_3Al_3O_9$, in particular.[39] The Ga-Al ratio influenced the alcohol-dehydrogenation capability of the catalysts and consequently the oxidation activity. This catalyst was also very active and selective in BA oxidation giving >99% selectivity to benzaldehyde without solvent or base (Table 2, entry 6). Remarkably, high BA conversion was obtained even at ambient temperature.



$Au\subset CeO_2$ TOF=12500 h^{-1}
Au/$Ga_3Al_3O_9$ TOF=25000 h^{-1}
Au/MIL-101 TOF=29300 h^{-1}

Scheme 4 Turn-over frequencies in the oxidation of 1-phenylethanol to acetophenone using gold supported on nano-ceria,[44] Ga-Al mixed oxide[39] and metal-organic frameworks (MIL-101).[42]

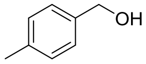
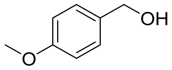
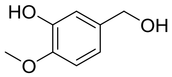
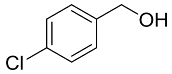
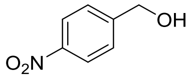
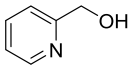
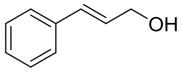
In some cases, solvent can be beneficial for the oxidation reaction. A Au/TiO_2 catalyst, prepared by deposition-precipitation, gave only 15% conversion and 65% selectivity to benzaldehyde in solvent-free BA oxidation.[35] Interestingly, the use of water as solvent promoted the oxidation, and conversion increased to 83%. Furthermore, the use of biphasic water/*p*-xylene increased selectivity to 93% (Table 2, entry 7). In the multiphase reaction system, organic solvent dissolves the produced benzaldehyde while the catalyst and BA are mainly in the aqueous phase, resulting in increased selectivity.

Support properties, such as acidity and basicity, have a significant effect on the selectivity of BA oxidation. Fang *et al.* compared gold supported on various materials in oxidant-free dehydrogenation of BA into benzaldehyde.[40] The highest activity and selectivity were observed with gold on hydrotalcite (HT), which had both strong acid and basic sites in the support (entry 8). The authors claimed that these sites play a key role in the oxidant-free dehydrogenation mechanism. In the presence of an oxidant however, Villa *et al.* showed that support basicity can increase overoxidation to benzoic acid and consequently decrease selectivity.[45]

In recent years, a great deal of research on gold catalysts has been concentrated on developing sophisticated support materials with tunable properties, such as zeolites[41] or metal-organic frameworks (MOFs).[42,46] Gold supported on microporous zeolite-Y oxidized BA with total selectivity to benzaldehyde, though addition of 1 equiv. K_2CO_3 was required for high conversion (Table 2, entry 9).[41] Moreover, the catalyst was reusable; the activity remained constant during five consecutive runs. Another interesting catalyst was developed by deposition of gold on MOF (MIL-101), a porous framework of chromium ions bridged by terephthalate.[42] The best catalyst, which also displayed the smallest Au particle size, was obtained by deposition of PVP-protected Au colloids on the support. The Au/MIL-101 catalyst oxidized BA quantitatively into benzaldehyde under very mild conditions (entry 10). Furthermore, activity of the catalyst in oxidation of 1-phenylethanol exceeded those previously reported (Scheme 4).

Various substituted benzyl alcohols and cinnamyl alcohol were also selectively oxidized into the corresponding aldehydes with Au/MIL-101 (Table 3). Substrates with electron-donating groups (entries 1-3) were more easily oxidized compared to those with electron-withdrawing groups (entries 4 and 5). Interestingly, 2-pyridinemethanol was oxidized with very high yield despite the nitrogen heteroatom, which might coordinate strongly to gold (entry 6).

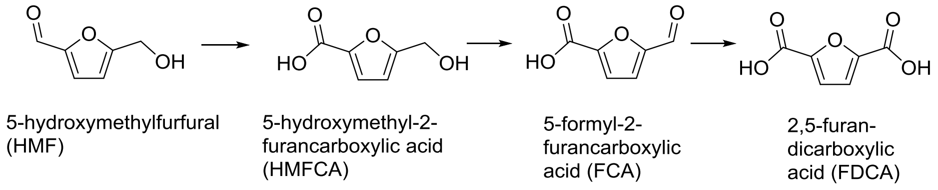
Table 3 Aerobic oxidation of aromatic alcohols to corresponding aldehydes with Au/MIL-101.[42]

Entry	Substrate	Time (h)	Conv. (%)	Sel. (%)
1		1	>99	>99
2		1	>99	>99
3		1.5	99	>99
4		2.5	99	99
5		5	95	99
6[a]		5	98	99
7		1	>99	>99

Reaction conditions: 1 mmol alcohol, 1 mol% Au, toluene as solvent, 80 °C, O_2 flow.
[a] 1.5 mol% Au.

3.1.3 Oxidation 5-hydroxymethylfurfural

Formed by dehydration of fructose and glucose, 5-hydroxymethylfurfural (HMF) is considered to be an important platform chemical for the production of renewable chemicals.[47] Oxidation of both the aldehyde and primary hydroxyl group of HMF produces 2,5-furandicarboxylic acid (FDCA) (Scheme 5), which has been suggested as a replacement for terephtalic acid in the production of polyethylene terephthalate (PET).[48] Generally, alkaline conditions are required to obtain the diacid in aqueous solution, which presents a challenge due to the instability of HMF at high pH.



Scheme 5 Intermediates of HMF oxidation.[16]

Before the advent of gold catalysis, oxidation of HMF was studied with Pt and Pd catalysts. Compared to Pt and Pd on carbon, the activity of Au catalysts Au/C and Au/TiO_2 at room temperature was an order of magnitude higher.[49] However, both Pt and Pd catalysts showed higher selectivity towards FDCA (79% and 71%, respectively) than Au (8%) after 6 h. Increasing oxygen pressure, amount of NaOH or reaction time increased FDCA selectivity up to 80% (Table 4, entry 1).

Corma's group studied HMF oxidation using gold supported on metal oxides.[50] The oxidation was greatly affected by the support, and gold on titania and nanoparticulate ceria displayed the highest activities. The aldehyde group of HMF was quickly oxidized in alkaline conditions giving 100% selectivity to HMFCA during the first hour of the reaction. Though oxidation of the primary hydroxyl group was considerably slower, high selectivities to FDCA were obtained with both Au/TiO_2 and Au/CeO_2 (Table 4, entries 2 and 3). At least 2 equiv. of NaOH was required to obtain high selectivity to the diacid (96% in 20 h with Au/CeO_2), corresponding to the amount needed to neutralize the acid groups in the product. Further increase in the amount of base resulted in faster reaction; 96% yield of diacid was achieved in 5 h with 4 equiv. of NaOH. However, recycling experiments showed strong deactivation of Au/CeO_2 due to adsorption of organic species on the catalyst.

Recently, the catalytic activity of Au/CeO_2 was improved by doping the ceria support with Bi.[51] Using a Au/$Ce_{0.9}Bi_{0.1}O_{2\text{-}\delta}$ catalyst, quantitative conversion to FDCA was achieved under mild conditions and shortened reaction time (Table 4, entry 4). Moreover, the catalyst showed improved stability and could be recycled up to three times with only minor decrease in FDCA selectivity. According to the study, the Bi-doping facilitated O_2 activation and dehydrogenation of the substrate by increasing the number of

Ce^{3+} centres and $Au^{\delta+}$ on the support, which were previously shown to be the active sites with gold on nano-ceria.[44]

Table 4 Oxidation of HMF into FDCA in aqueous solutions with gold catalysts.

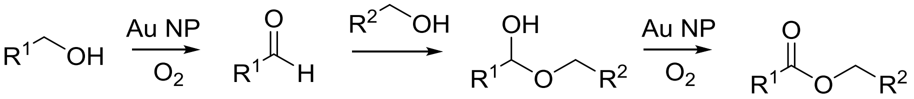
Entry	Catalyst	HMF: Au	NaOH equiv.	Conditions	Conv. (%)	Sel. (%)	Ref.
1	Au/TiO_2	125	20	20 bar O_2, 22 °C, 22 h	100	80	49
2	Au/TiO_2	640	4	10 bar air, 130 °C, 8 h	99	84	50
3	Au/CeO_2	640	4	10 bar air, 130 °C, 5 h	99	96	50
4	$Au/Ce_{0.9}Bi_{0.1}O_{2-\delta}$	150	4	10 bar O_2, 65 °C, 2 h	100	>99	51
5	Au/HY	110	4	3 bar O_2, 60 °C, 6 h	>99	>99	52
6	Au/HT	40	-	O_2 flow, 95 °C, 7 h	>99	>99	53

Cai *et al.* studied zeolite supported gold catalysts in HMF oxidation; 99% FDCA yield was achieved with gold on acidic HY zeolite (entry 5).[52] The Au NPs were confined inside the HY zeolite supercage resulting in very narrow particle size distribution and mean particle size of 1 nm. On less acidic supports, Au particles transferred to the surface of the zeolites resulting in growth of particle size. The stabilizing effect of the HY zeolite was also observed upon catalyst recycling; no sintering was occurred, and furthermore, high FDCA yields were obtained with the reused catalyst.

The need for excessive amount of base with gold catalysts is a major disadvantage both environmentally and economically, as large amounts of waste are generated during acidification and purification of the product. Therefore, there is growing interest in base-free HMF oxidation despite the low solubility of FDCA in neutral water.[53] Using gold supported on hydrotalcite, a layered Mg/Al hydroxide, >99% yield of FDCA was obtained without the addition of homogeneous base (entry 6). The authors claimed that the basic support replaces the need for additional base. However, concerns were raised that Mg^{2+} from the HT support[54] or residues of alkali salts used in preparation of the support might act as sacrificial base by leaching into the acidic solution.[55] Further studies showed that Au/HT, carefully prepared without alkali salts, could indeed catalyse the base-free HMF oxidation, though the reaction showed unexpected sensitivity to the amount of surface gold.[55] In the absence of base, HMF adsorbs strongly on gold blocking the active sites and therefore, high concentrations of gold were required to achieve high yields of FDCA.

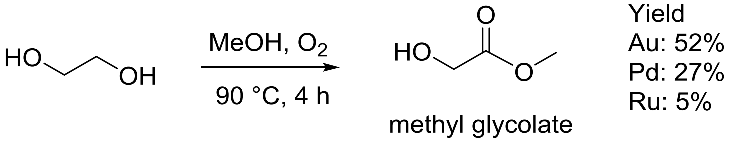
3.1.4 Oxidative esterification

Esters have been observed as side products or even main products in gold catalysed oxidation of alcohols; solvent-free oxidation of 3-phenyl-1-propanol with Au/CeO_2 gave 98% selectivity to 3-phenylpropanol-3-phenylpropanoate.[44] The ester formation was proposed to proceed through formation of hemiacetal from the intermediate aldehyde (Scheme 6). Similarly in water, hydroxide ion attacks the aldehyde forming a geminal diol, and subsequent oxidation of the diol gives carboxylic acid as the product. Participation of the solvent can be utilized in synthesis of methyl esters by oxidation of alcohols in methanol. Methanol itself is resistant towards oxidation, permitting its use as solvent. Accordingly, oxidation of 1-hexanol and BA in methanol with Au/TiO_2 gave the corresponding methyl esters with over 90% yields.[56] As an advantage, the need for stoichiometric amount of base to neutralize acidic products is avoided, though catalytic amounts of e.g. sodium methoxide have been used to accelerate the reaction. In some cases, the methyl ester can be a more desirable product than the corresponding carboxylic acid. For instance, FDCA, the product of aqueous oxidation of HMF has limited solubility in water, whereas the corresponding dimethyl ester is readily soluble in methanol.[57]



Scheme 6 Proposed mechanism for ester formation with gold catalysts.[44]

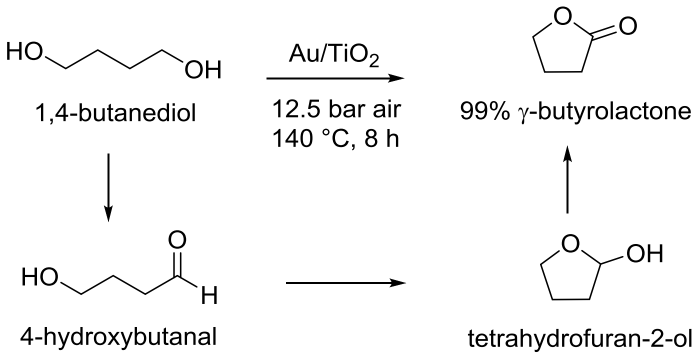
Oxidative esterification combined with the selectivity towards monooxidation of diols gave one of the earliest industrial applications of gold catalysts; production of methyl glycolate by oxidation of ethylene glycol in methanol.[58] Methyl glycolate is used e.g. as solvent in semiconductor manufacturing or in cosmetics. Gold was clearly more active and selective compared to Pd and Ru catalysts (Scheme 7).



Scheme 7 Oxidative esterification of ethylene glycol with methanol by Au, Pd and Ru supported on alumina.[58]

The oxidative esterification of glycerol is challenging due to the complex oxidation pathways already observed in aqueous solutions. Using a Au/TiO_2 catalyst in methanol, 82% selectivity to methyl glycerate at 72% conversion was obtained with the addition of 10 mol% NaOMe.[59] Under base-free conditions, higher conversion was obtained, but selectivity to methyl glycerate was only 50% due to formation of dimethyl mesoxalate as side product. In a recent study, glycerol was converted directly to methyl lactate (73% yield) using gold supported on an acidic zeolite catalyst in methanol.[60] Gold was responsible for the initial oxidation of glycerol to glyceraldehyde and the zeolite support for further conversion to methyl lactate. The catalyst could be reused without loss of activity or selectivity, giving an attractive one-pot route to an important renewable chemical.

In the case of diols with at least four carbons, selective oxidation can produce lactones *via* cyclization. Oxidation of 1,4-butanediol with Au/TiO_2 gave 99% γ-butyrolactone when inert tributyl phosphate was used as solvent (Scheme 8).[61] After oxidation of one hydroxyl group, the other hydroxyl group attacks the aldehyde forming an intermolecular hemiacetal, which is further dehydrogenated to the lactone. Interestingly, γ-butyrolactone was the main product even if the oxidation was carried out in methanol.[62]



Scheme 8 Oxidative cyclization of 1,4-butanediol to γ-butyrolactone with Au/TiO_2.[61]

3.2 Oxidation of aldehydes and carbohydrates

3.2.1 Oxidation of aldehydes

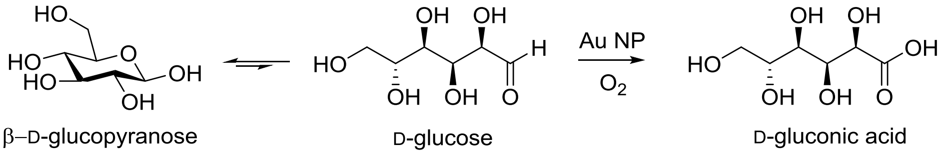
Aldehydes are generally rather reactive towards oxidation and milder conditions or shorter reaction times are needed compared to alcohols. However, only a handful of reports on gold-catalysed aldehyde oxidation have been published, in contrast to the extensive research on alcohol oxidation. Using Au/C catalyst in aqueous solution, aliphatic aldehydes were oxidized into acids with over 90% yields in 2 h without additional base.[63] The catalyst was reused four times without change in activity. In comparison, Pt/C gave similar activity in the first run, but 40% of its activity was lost upon recycling. CCl_4 was an even better solvent also enabling fast oxidation of water-insoluble aldehydes, while acetonitrile inhibited the reaction. Benzaldehyde was oxidized with 96% conversion in CCl_4, whereas *ortho-* and *para*-hydroxybenzaldehydes were unreactive.

Corma and Domine studied Au/CeO_2 catalysts as well as homogeneous Mn(II)-, Co(II)- and Ni(II) acetates in oxidation of *n*-heptanal.[64] Gold supported on meso-structured nanocrystalline ceria gave 95% yield of heptanoic acid in 3.5 h at 50 °C with flowing air as oxidant. Compared to the metal acetates, turn-over numbers (TON) of gold were over six times greater. Interestingly, the Au/CeO_2 catalyst was active in acetonitrile, and moderate activity was also achieved in solvent-free oxidation.

Oxidative esterification of aldehydes in methanol was particularly fast; benzaldehyde was quantitatively converted to methyl benzoate in one hour at ambient conditions using 0.2 mol% Au/TiO_2 and 10 mol% NaOMe.[65] The oxidation proceeded even at –78 °C, and over 50% conversion was obtained in 4 h at –20 °C. In the absence of base, however, the oxidation slowed down and completion took over 30 h. In addition to methanol, over 80% yields to the corresponding esters were obtained in ethanol, 1-propanol and benzyl alcohol in 20 h.

3.2.2 Oxidation of glucose

The selective oxidation of D-glucose into gluconic acid with gold was first described shortly after the early reports on oxidation of diols. In neutral water, the most common tautomers of glucose are the cyclic forms, such as β-D-glucopyranose.[66] A minor amount of glucose is also in the open chain form, allowing oxidation of the aldehyde group to give gluconic acid (Scheme 9). Using Au/C, glucose was quantitatively oxidized in mild conditions at pH 9.5 (Table 5, entry 1).[67] Surprisingly, Au/C was several times more active compared to commercial bismuth-doped carbon-supported Pd and Pd-Pt catalysts, specifically designed for glucose oxidation. Carbohydrates are sensitive to isomerization and degradation under highly alkaline conditions, and to avoid the use of excess base, constant pH was maintained by continuous addition of NaOH.[67] Consequently, gluconate salt is the product. Even though base increased the oxidation rate, Au gave full conversion at pH 7-8 and even without pH control, while both Pd and Pd-Pt deactivated under these conditions before the oxidation was complete. After this seminal study, glucose oxidation has been extensively investigated, and relevant results are presented in Table 5.



Scheme 9 Possible tautomers of glucose and its oxidation to gluconic acid.

Table 5 Oxidation of glucose into sodium gluconate with gold catalysts.

Entry	Catalyst	Glc:Au	pH	Conditions	TOF (h^{-1})[a]	Sel. (%)	Ref.
1	Au/C	1000	9.5	O_2 flow, 50 °C	13000[b]	>99	[67]
2	Au sol	4000	9.5	O_2 flow, 30 °C	50000	>99	[68]
3	Au/C	40000	9.5	O_2 flow, 50 °C	150000	>98	[69]
4	Au/TiO_2	11000	11	O_2 flow, 60 °C	10000 [b]	98	[70]
5	Au/Al_2O_3	-	9	O_2 flow, 40 °C	22000 [b]	>99	[71]
6	Au/ZrO_2	32000	9.5	O_2 flow, 50 °C	200000	>98	[72]

[a] TOF values are based on available surface metal. [b] The TOF value reported in the reference was based on total metal, so a re-calculated value by Davis *et al.*[16] is given.

Colloidal solution of unsupported and unprotected Au nanoparticles was highly active in glucose oxidation, giving 21% conversion after 200 s reaction (Table 5, entry 2).[68] Under similar conditions, nanoparticles of copper, silver, palladium and platinum showed hardly any activity. However, the naked Au particles coagulated and deactivated rapidly during the oxidation. Similar initial activity, as well as longer catalyst lifetime, was achieved by supporting the particles on carbon. This illustrates the importance of support in stabilizing the nanoparticles, though in this case the catalytic activity clearly originated from gold alone. For particles smaller than 6 nm, the oxidation activity was inversely proportional to the diameter, while larger particles were considerably less active.

Structure sensitivity of glucose oxidation was studied with Au/C catalysts, prepared by immobilizing particles with mean diameters 3-6 nm on the carbon support.[73] The initial oxidation rates showed exponential dependence on the specific surface area of gold, indicating that only the surface gold is active in the reaction. Optimization of Au/C catalyst preparation[74] and reaction conditions increased the oxidation rate significantly, giving an extremely high TOF value of 150000 h^{-1} (entry 3).[69] Remarkably, the activity is comparable to enzymatic oxidation of glucose, used in the industrial process for preparation of gluconic acid. Despite the outstanding activities, deactivation of Au/C catalysts upon recycling has been reported.[67,69] Biella *et al.* observed that the deactivation was dependent on pH of the reaction; the decrease of activity was more pronounced at low pH (7-8).[67] Accordingly, gold leaching was detected at pH 7-8, though increase in gold particle size occurred regardless of pH.

In order to improve the long-term stability of gold catalysts, Prüße's group studied gold supported on metal oxides, such as Al_2O_3 and TiO_2.[70,71,75] Gold supported on titania using deposition-precipitation method gave very high selectivities and activities in glucose oxidation (entry 4).[70] Under optimized conditions, the catalyst was successfully reused in 17 consecutive runs without loss of activity. Similar results were obtained with alumina supported catalysts; high TOF values up to 22000 h^{-1} were achieved with Au/Al_2O_3 prepared by incipient wetness method (entry 5).[71] In 18 repeated experiments using an industrially relevant glucose concentration (30 wt%), the catalyst showed no deactivation. Furthermore, the catalyst was used for 110 days in continuous-flow glucose oxidation without loss of performance.[75]

With high glucose concentrations and increasing catalyst activities, the low solubility of oxygen in water can be a limiting factor on the oxidation rate. To avoid these mass transfer limitations, Saliger *et al.* studied glucose oxidation with hydrogen peroxide as oxidant instead of oxygen or air.[76] Using Au/Al_2O_3 prepared by incipient wetness method, activities over 8000 mmol min^{-1} g_{Au}^{-1} were achieved with H_2O_2, while oxygen bubbling gave 1880 mmol min^{-1} g_{Au}^{-1} activity under similar conditions.[71] Total selectivity to sodium gluconate was reported with both methods. Gold catalysts decompose hydrogen peroxide *via* intermediate peroxo and superoxo species into dioxygen.[76] In fact, the effective oxidizing agent in the reaction is a species formed by the decomposition, not H_2O_2 itself.

Haruta's group reported a very simple but efficient solid grinding method for preparing gold catalysts; a volatile organogold complex and metal oxide or carbon support were mixed in a ball mill without any solvent, and subsequently calcined to reduce the gold precursor.[72] The method was suitable for nonreducible supports, such as zirconia and alumina, giving small Au particles with a mean diameter of 2-3 nm. Accordingly, Au/ZrO_2 and Au/Al_2O_3 prepared by this method gave extremely high TOF values up to 200000 h^{-1} in glucose oxidation, the highest activities reported so far (Table 5, entry 6).

3.2.3 Base-free oxidation of glucose

Currently, the oxidation of glucose to gluconic acid requires the addition of base with both noble metal catalysts and the commercially used enzymes to prevent deactivation. To avoid the need for base as well as the strong acid used to isolate the product, there is growing interest in base-free glucose oxidation. Early studies showed that Au/C is also able to oxidize glucose without pH control, but pressurized oxygen, high temperature and increased reaction time were required (Table 6, entry 1).[67] Furthermore, the acidic conditions promoted gold leaching, and the catalyst lost 70% Au during six consecutive runs. Apparently, increased catalyst stability and activity under acidic conditions are required to enable the direct production of free gluconic acid. Recently, the topic has been studied by several groups, and the results are presented in Table 6.

Table 6 Base-free oxidation of glucose into gluconic acid.

Entry	Catalyst	Glc:Au	Conditions	Conv. (%)	Sel. (%)	Ref.
1	Au/C	1000	3 bar O_2, 100 °C, 6 h	100	100	[67]
2	$Au/nCeO_2$	140	2.3 bar O_2, 65 °C, 2 h	74	95	[77]
3	Au/MgO	1600	air, 60 °C, 24 h	57	100	[78]
4	Au/CMK-3[a]	1000	3 bar O_2, 110 °C, 2 h	92	88	[79]

[a] Gold on mesoporous carbon.

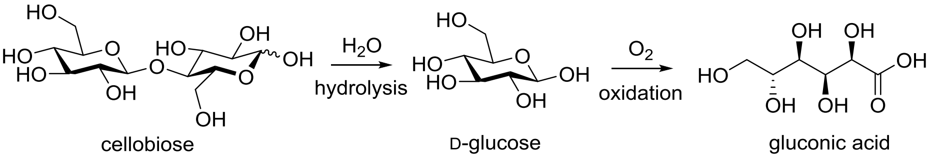
Wang *et al.* studied base-free oxidation of glucose using gold supported on nano- and microcrystalline ceria.[77] Similar conversion and selectivity was observed with both catalysts (entry 2), but Au on nanosized ceria showed higher resistance towards deactivation upon recycling. Notably, $Au/\mu CeO_2$ lost 55% of gold during five reaction cycles, whereas $Au/nCeO_2$ lost only

2%. Furthermore, Au particle sintering was more pronounced on the microcrystalline support. As the surface area of the nanocrystalline support was 25 times larger compared to microcrystalline ceria, the authors proposed that the stability of the catalyst was related to the surface density of Au particles. Long interparticle distance prevents coalescence of the NPs and, in addition, $nCeO_2$ has more anchoring sites which can stabilize the particles. Indeed, lowering the Au loading on μCeO_2 to achieve surface density similar to $Au/nCeO_2$ gave a very active catalyst with initial TOF value of 3100 h^{-1}. Nevertheless, deactivation of the catalyst due to adsorption of organic species was observed, and attempt to regenerate the catalyst by calcination led to Au sintering and decreased activity.

The use of basic support to replace the sacrificial base was studied by Hutchings' group.[78] With gold supported on magnesia, glucose was oxidized in mild conditions using ambient air as oxidant, and total selectivity to gluconic acid was reported (entry 3). However, hydration of the magnesia support to $Mg(OH)_2$ resulted in minor leaching of Mg^{2+} to the acidic solution. Similar leaching was observed in base-free glycerol oxidation with MgO supported catalysts.[80] Furthermore, adsorbed organic species were detected on the support, and similar to the previous study on Au/CeO_2, the activity could not be restored by catalyst calcination.

Mesoporous carbon CMK-3 consisting of ordered hexagonal channels was used as support for Au NPs.[79] The Au/CMK-3 catalyst gave very high initial activities over 17000 h^{-1} in base-free glucose oxidation (entry 4). With Glc:Au ratio at 100, 92% yield of gluconic acid was obtained in 15 min. Recycling studies showed a moderate decrease in performance; conversion dropped from 92% to 70% in the fourth run. In this case, no sintering of the particles was observed; the Au particles were confined inside the channels of the support, allowing diffusion of substrate and product but preventing sintering of the Au NPs. Analysis of the used catalyst revealed increase of carboxylic acids and hydroxyl functionalities on the carbon support; 30% mass loss was observed upon calcination. Catalyst regeneration by washing with NaOH removed the adsorbed species, and 87% conversion was achieved with the treated catalyst.

Base-free glucose oxidation is a crucial step towards direct, one-pot conversion of cellulose to gluconic acid through acid hydrolysis followed by catalytic oxidation. Cellulose is the most abundant source of glucose, but its hydrolysis is challenging due to the β(1→4)-glycosidic bond between the glucose units. The conversion has been studied with cellobiose, a dimer of glucose, as model compound and gold nanoparticles on acidic supports as catalysts. The acidic support is proposed to catalyse hydrolysis of the β-glycosidic bond, while gold oxidizes glucose into gluconic acid (Scheme 10).[81] Wang's group studied cellobiose oxidation using various catalysts in water without pH control. High temperature and oxygen pressure were required for the conversion. The highest conversion and selectivity to gluconic acid were obtained with gold supported on carbon nanotubes (CNT) (Table 7, entry 1).[82] Pretreatment of the support with concentrated HNO_3 increased acidic carboxyl and hydroxyl groups on the CNT surface. The support acidity accelerated the hydrolysis of cellobiose, as well as increased selectivity, by suppressing further oxidation of gluconic acid.



Scheme 10 Conversion of cellobiose into gluconic acid.

Table 7 Oxidation of cellobiose (CB) into gluconic acid with gold catalysts.

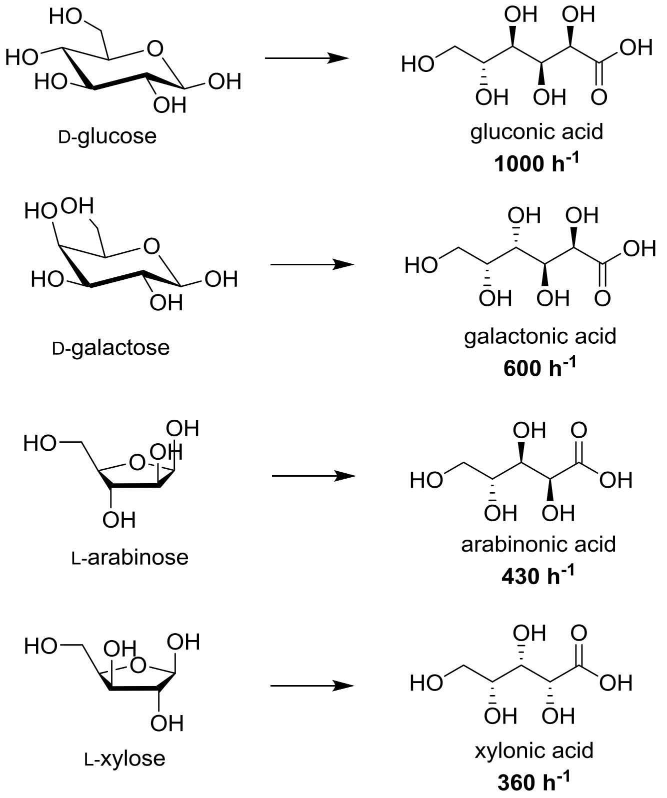
Entry	Catalyst	CB: Au	Conditions	Conv. (%)	Sel. (%)	Ref.
1	Au/CNT	240	5 bar O_2, 145 °C, 3 h	81	84	[82]
2	$Au/Cs_2HPW_{12}O_{40}$	120	5 bar O_2, 145 °C, 3 h	98	99	[81]
3	$Au/Cs_{1.2}H_{1.8}PW_{12}O_{40}$	120	5 bar O_2, 145 °C, 3 h	97	>99	[83]

Similar effect of support acidity was observed with gold supported on cesium hydrogen phosphotungstates, which are insoluble acidic polyoxometalates.[81,83] Almost complete conversions and 99% selectivities to gluconic acid were achieved (entries 2 and 3). The catalysts showed minor deactivation upon recycling, though conversion and selectivity remained >90% after five runs.[83] The $Au/Cs_{1.2}H_{1.8}PW_{12}O_{40}$ catalyst was also able to directly convert cellulose into gluconic acid with 60% yield in 11 h. However, the prolonged reaction time led to catalyst deactivation due to leaching of phosphotungstic acid $H_3PW_{12}O_{40}$ into the solution. A more durable catalyst system was obtained by using a mixture of $Au/Cs_3PW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, which could be recovered from the reaction mixture and recycled; cellulose was converted to gluconic acid with 66% yield even after six reuses.

3.2.4 Oxidation of other sugars

Glucose is the most abundant monosaccharide, and therefore, it is the most studied substrate for selective oxidation. However, numerous other monosaccharides are available from hemicelluloses, a group of heterogeneous polysaccharides accounting for 20-35% of lignocellulosic biomass.[15] Hemicelluloses are currently underutilized in wood-based biorefineries and they can be easily hydrolysed into monosaccharides using mild acids, which makes them a very appealing feedstock for renewable chemicals.[84] Common monosaccharides in hemicelluloses include L-xylose, L-arabinose, D-galactose, D-mannose and D-glucose. Several studies have shown that gold catalysts oxidize the aldehyde group of these saccharides with exceptional selectivity, though the activities vary depending on the catalyst and substrate structure.

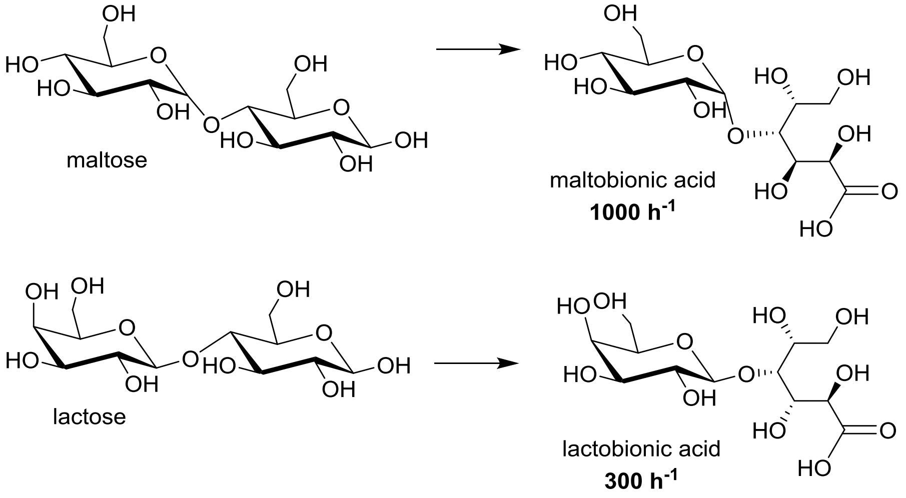
Mirescu *et al.* compared Au, Pd and Pt catalysts in oxidation of various carbohydrates at mildly alkaline conditions in water.[85] In the case of both hexoses and pentoses, Au/TiO_2 catalyst gave total conversion and very high >99% selectivities to the corresponding aldonic acids at pH 9 and 40 °C (Scheme 11). The selectivities of Pd and Pt supported on alumina varied depending on the substrate between 70-95%. In addition, Au was several times more active compared to Pd and Pt, regardless of the substrate. The highest activity with gold was observed in oxidation of glucose, while galactose, differing only in orientation of the hydroxyl at C_4, oxidized more slowly. Interestingly, the Pd and Pt catalysts showed opposite behaviour with the two hexoses. The pentoses arabinose and xylose were oxidized with similar activities using Au/TiO_2, though both slower than the hexoses.



Scheme 11 Oxidation of hexoses and pentoses to corresponding aldonic acids using Au/TiO_2 at pH 9 and 40 °C.[85] TOF values at 10% conversion were re-calculated based on available surface metal by Davis *et al.*[16]

Further studies by Murzin's group showed that Au/Al_2O_3 was the most suitable catalyst for oxidation of arabinose and galactose.[86-88] With both substrates, the effect of Au particle size on the activity was studied, and maxima at 2.3 nm and 2.6 nm mean particle sizes were found for oxidation of arabinose[87] and galactose,[88] respectively. Selectivity was not affected by the particle size, and the corresponding aldonic acids were produced with >99% selectivities at 99% conversions at pH 8 and 60 °C.

In addition to monosaccharides, disaccharides such as maltose and lactose are interesting substrates for selective oxidation.[15] In mildly alkaline conditions, selective oxidation of the aldehyde group of the reducing end occurs without hydrolysis of the glycosidic bond, e.g. cellobiose is oxidized into cellobionic acid.[85] Using Au/TiO_2, lactobionic acid and maltobionic acid were also produced with very high selectivities (Scheme 12). Maltose, consisting of two glucose units linked by an α-glycosidic bond, was oxidized with similar activity as glucose, while the presence of galactose unit decreased the rate of lactose oxidation. With Pd catalysts, selectivity to lactobionic acid decreased due to consecutive oxidation to 2-keto-lactobionic acid, which highlights again the advantage of gold catalysts in oxidation of carbohydrates.[89]

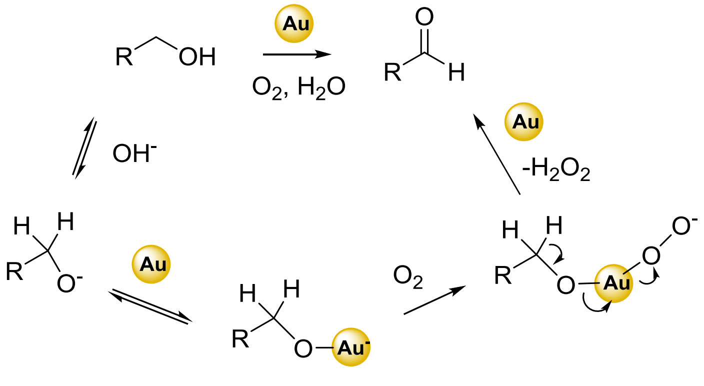


Scheme 12 Oxidation of lactose and maltose using Au/TiO_2 at pH 9 and 40 °C.[85] TOF values re-calculated based on available surface metal by Davis *et al.*[16]

3.3 Oxidation mechanism

The oxidation of alcohols and aldehydes using noble metal catalysts is thought to proceed *via* an oxidative dehydrogenation mechanism.[16,22,90] However, early studies with polymer stabilized Au and Pd showed marked differences in the behaviour of the two metals regarding the role of oxygen and hydroxide ion.[34] Oxidation of alcohols with Au required the presence of base, whereas Pd catalysts do not necessarily require additives.[10] The first step of the oxidation is activation of alcohol by deprotonation, which can occur either on the metal surface or in solution and is greatly accelerated in alkaline solution. Theoretical calculations by Zope *et al.* showed that the activation barrier for dissociative adsorption of aqueous ethanol on clean Au surface was very high (204 kJ/mol), but the presence of surface-bound hydroxide intermediates decreased the barrier to 22 kJ/mol.[24] Alternatively, hydroxide ions can deprotonate the alcohol already in solution phase facilitating the adsorption of alkoxide on the metal. The surface-bound alkoxide is then dehydrogenated to form a carbonyl species and metal-hydride.[91] A large kinetic isotope effect was found in oxidation of deuterated *p*-hydroxybenzyl alcohol, indicating that the C–H bond activation is a likely rate-determining step in alcohol oxidation.[34]

The carbonyl compound forms without incorporation of molecular oxygen, however O_2 is needed to remove the electrons deposited on the metal.[24] Experimental evidence show that hydrogen peroxide is formed as the reduction product, suggesting that O_2 is associatively adsorbed on the gold surface (Scheme 13).[92,93] During glucose oxidation on colloidal gold, H_2O_2 was detected at the start of the reaction in stoichiometric ratio with respect to the produced gluconate.[93] However, during prolonged reaction or at high pH, H_2O_2 decomposed and lower amounts were detected; alkaline conditions and metals are known to catalyse H_2O_2 decomposition.[94] Zope *et al.* proposed that oxygen activation by gold could lead to regeneration of hydroxide ions through dissociation of the formed H_2O_2 (Equations 1-3).[24] More recently, theoretical studies on metal surfaces confirmed that Au(111) is unable to dissociatively adsorb O_2, whereas the dissociation was favourable on Pd(111) and Pt(111).[95]



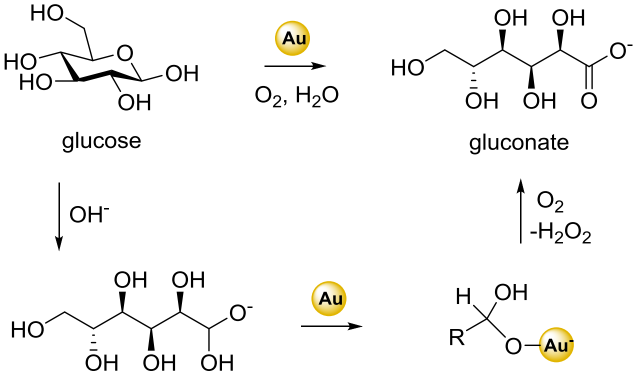
Scheme 13 Mechanistic model for aerobic alcohol oxidation, proposed by Comotti *et al.*[93]

$$O_2 + H_2O \rightarrow OOH + HO \quad (1)$$

$$OOH + H_2O \rightarrow H_2O_2 + HO \quad (2)$$

$$HO + e^- \leftrightarrow HO^- \quad (3)$$

In alkaline aqueous solution, aldehydes and carbohydrates are readily oxidized further into carboxylic acids. Isotope studies on oxidation of ethanol, glycerol and HMF have shown that the oxygen atoms in the produced acid originate from water, not from O_2.[24,96] This suggests that the aldehyde group is hydrated by hydroxide ion from water to form a geminal diol. The deprotonated diol adsorbs on the metal surface, and carboxylic acid forms through dehydrogenation similarly to alcohol oxidation (Scheme 14). The isotope studies found multiple labelled O atoms incorporated into the products, which is explained by rapid exchange of the hydroxyl groups of the diol. Accordingly, the increased hydroxide concentration at high pH accounts for increased oxidation rates.



Scheme 14 Mechanism for glucose oxidation with gold.[73,93]

Hydroxide ions have another important role in aqueous oxidation, in addition to deprotonating the alcohol and hydrating the aldehyde; neutralizing the produced carboxylic acid.[73] Free carboxylic acids adsorb strongly on gold surface blocking active sites and deactivating the catalyst. In alkaline media however, deprotonated acid readily desorbs the catalyst surface. An especially strong inhibiting effect was found with ketones or compounds having secondary hydroxyl groups which can produce ketones under oxidative conditions, such as sugar acids and polyols.[28] The strong inhibition was explained by chelation of the species on the metal surface.

3.4 Bimetallic gold catalysts

Doping gold catalyst with a second metal can improve the properties of the catalyst even further. Many of the recent advances in gold catalysis are related to the use of bimetallic or trimetallic nanoparticles. Gold-palladium and gold-platinum catalysts are the most extensively studied, owing to the similar applications and miscibility of the metals.[97] Numerous studies report superior performance of heterometallic catalysts compared to those based on the constituent metals alone; improved catalytic activity, selectivity to the desired product and catalyst stability have been observed. Development of high resolution characterization techniques, such as scanning transmission electron microscopy (STEM), have allowed detailed study of the morphology of the nanoparticles.[98] The synergistic effects have been ascribed to modification of the electronic structure by *e.g.* electronic charge transfer, or to structural changes in the metal surface, though in many cases the reasons are not completely understood.[99] The use of gold-containing bimetallic and trimetallic catalysts has been recently reviewed,[16,97,99] and therefore only a few illustrating examples are given here.

Synergistic effects of gold and palladium were shown in solvent-free oxidation of aromatic and aliphatic alcohols using Au-Pd/TiO_2.[100] Oxidation of benzyl alcohol with monometallic Au or Pd catalyst gave low selectivity, but the bimetallic catalyst was both more active and more selective. Furthermore, an extremely high activity close to 270000 h^{-1} was achieved in oxidation of 1-phenylethanol, almost an order of magnitude higher than reported with monometallic gold catalysts (*cf.* Scheme 4). Characterization of the catalyst showed that the catalyst surface was significantly enriched with Pd.

The need for base with gold catalysts is a major disadvantage, and several studies have employed bimetallic systems to overcome this limitation. Early studies on oxidation of glucose without pH control showed that addition of Pt to Au/C increased the activity from 51 h^{-1} to over 900 h^{-1}.[101] Interestingly, similar synergistic effect was not observed in alkaline conditions, as both the monometallic and bimetallic catalysts gave similar activities. Combining Au and Pt has also enabled advances in base-free oxidation of glycerol.[80,102] Villa *et al.* deposited Au-Pt nanoparticles on H-mordenite, achieving 83% selectivity to glyceric acid at 70% conversion (3 bar O_2, 100 °C, 2 h).[102] Compared to carbon supported catalyst, formation of H_2O_2 was avoided with the acidic zeolite support, preventing C–C scission. Hutchings' group achieved base-free glycerol oxidation in mild conditions with Au-Pt supported on alkaline magnesia.[80] At 60 °C, 43% conversion and 72% selectivity to glyceric acid were obtained. Remarkably, glycerol was also oxidized in ambient temperature with 85% selectivity to glyceric acid. In case of base-free glucose oxidation however, addition of Pd to Au/MgO gave only a minor improvement in the activity; 57% and 62% conversions to gluconic acid were obtained with monometallic and bimetallic catalysts, respectively.[78]

4 Results and discussion

4.1 Experimental notes

Detailed experimental data can be found in the publications attached and related supporting material available on the publishers' webpages.

4.1.1 Catalyst preparation and characterization

Gold catalysts were prepared by depositing gold precursor $HAuCl_4$ on metal oxide supports using two previously reported methods. Direct ion-exchange method (DIE) was used to prepare Au/Al_2O_3-DIE.[103] Deposition-precipitation with urea (DPU) was applied for Al_2O_3, TiO_2, $MgAl_2O_4$ and MgO.[27,104,105] The $MgAl_2O_4$ spinel support was prepared by coprecipitation.[27] The following metal oxide supports were purchased: Al_2O_3 (Alfa Aesar, γ-phase, 40 µm, S.A. 200 m^2/g), TiO_2 (Sigma-Aldrich, >95% anatase, <44 µm, S.A. 9 m^2/g) and MgO (Sigma-Aldrich, 99%). The preparation and characterization of Au/Al_2O_3 catalyst used in Publication I was carried out by Simakova *et al.*[87]

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD), atomic absorption spectrophotometry (AAS) and thermogravimetric analysis (TGA) techniques were applied in catalyst characterization. Gold dispersion was calculated from the particle size distribution as reported by Delidovich *et al.*[106]

4.1.2 Oxidation experiments

Oxidation experiments were carried out with different procedures depending on the substrate and oxidant. Oxidations under oxygen pressure were carried out in a steel autoclave loaded with glass liners, enabling up to 12 parallel reactions.[I,IV] Oxygen bubbling (100 ml/min) was applied for oxidations at controlled pH.[II] Microwave-assisted oxidations were carried out in glass vials using hydrogen peroxide as oxidant.[III]

Products were analysed and quantified using GC, GC/MS, HPLC and NMR (^{1}H, ^{13}C) techniques. To evaluate catalytic activity, turn-over frequencies (TOF) were calculated per surface Au atom[II-IV] from the conversion according to

$$TOF = \frac{n_{substrate}c}{n_{Au}D_{Au}t}$$

where $n_{substrate}$ is the number of moles of the substrate, c is conversion, n_{Au} is number of moles of gold, D_{Au} is dispersion, and t is time. In Publication I, TOF value was calculated based on total gold amount.

4.2 Catalyst properties

During the course of this work several metal oxide supported gold catalysts were prepared and characterized (Table 8). Metal oxides were selected as supports for their stability and the high activities presented in oxidation reactions.[44,70] The Au/Al_2O_3-DIE-1 catalyst used in Publication I was prepared and characterized by Prof. Murzin's group.[87] Two preparation methods were applied, DIE and DPU, both sharing the same the principle; $HAuCl_4$ precursor is deposited on the support and gold is reduced into metal nanoparticles using thermal treatment in air. In the DIE method, chloroauric anions adsorb on the hydroxyl groups present on the oxide surface.[103] The remaining chlorides are removed by washing with ammonia to prevent sintering or decreased activity.[107] In the DPU method, pH of the solution gradually increases due to decomposition of urea at high temperature, which leads to hydrolysis of the gold precursor and subsequent adsorption on the support.[104]

Characterization of the catalysts revealed considerable differences in the mean particle size and consequently gold dispersion (Table 8). The two Au/Al_2O_3-DIE catalysts (entries 1 and 2), exhibiting 1.0 nm and 2.4 nm mean diameters, were prepared by different groups using supports by different suppliers which might account for the difference. Similar mean size of Au particles (2.8 nm) was observed in the case of Au/Al_2O_3-DPU (entry 3). Particle size analysis of the Au/$MgAl_2O_4$ catalyst revealed a bimodal distribution; TEM analysis showed small Au particles with a mean diameter

3.8 nm whereas very large particles with sizes over 100 nm were detected with FESEM (entry 4).[III] Au/TiO_2 showed a slightly larger particle size (entry 5). Nonetheless, the particle size of all catalysts is well in the required range for catalytic activity.

Table 8 Properties of the catalysts used in this work.

Entry	Catalyst	Au loading (wt%)	d (nm)	Dispersion	Publication
1	Au/Al_2O_3-DIE-1	1.5	1.0 ± 0.3	0.77	I, [87]
2	Au/Al_2O_3-DIE-2	1.8 ± 0.15	2.4 ± 0.6	0.43	II, III, IV
3	Au/Al_2O_3-DPU	1.9 ± 0.03	2.8 ± 0.6	0.37	IV
4	Au/$MgAl_2O_4$	2.3 ± 0.12	3.8 ± 1.0[a]	0.27	III
5	Au/TiO_2	1.9 ± 0.04	4.6 ± 2.0	0.18	IV

[a] Also large (>100 nm) particle detected with SEM.

4.3 Oxidation of benzyl alcohol[I]

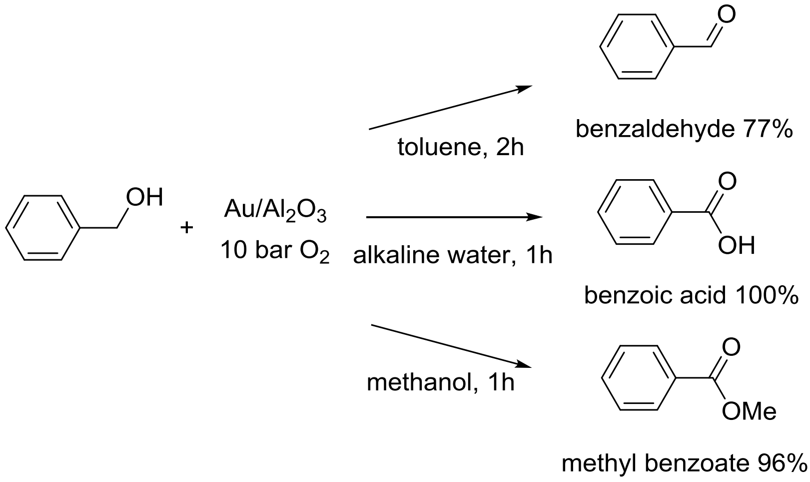
We initiated the studies on gold catalysed oxidation with benzyl alcohol as it is often used as a model substrate in oxidation reactions to probe catalytic reactivity.[16] Several reports on gold catalysed benzyl alcohol oxidation were published at the time of the study.[22] Using different catalysts and reaction conditions, benzaldehyde,[37] benzoic acid[108] as well as benzyl benzoate[35] were reported as main products. Our aim was to clarify the effect of different reaction conditions on the oxidation and gain control on the selectivity of the catalyst.

Initial studies with Au/Al_2O_3-DIE catalyst showed that in pure water the oxidation is unselective and slow. Changing the solvent to toluene gave high selectivity to benzaldehyde (89%). Also, the activity observed in toluene was higher than in pure water, likely due to the higher solubility of oxygen in toluene.[109] In further experiments we studied the catalyst in biphasic water-toluene systems. Compared to the oxidation in pure water, biphasic solvent significantly increased the conversion and selectivity toward aldehyde. The product is more soluble in toluene than in water, which might account for the low amount of side products even in the presence of water.

Additional base was reported to promote gold catalysed oxidations,[110] and therefore the addition of potassium carbonate and sodium hydroxide to the reaction was investigated. A nearly 10-fold increase in activity, resulting in full conversion, was observed with both bases. Moreover, alkaline conditions also promoted the subsequent oxidation of benzaldehyde to benzoic acid and very high selectivity to the acid was obtained using 1 equiv. NaOH in water and biphasic media. In contrast, benzoic acid was obtained only with moderate selectivity in toluene, indicating that the presence of water in addition to base is essential in the second step of the oxidation. Surprisingly, the highest activity of benzyl alcohol oxidation, over 5000 h^{-1}, was observed in alkaline biphasic solvent. This improved activity may be explained by the increased solubility of oxygen in toluene, in addition to the promoting effect of base.

At the time of the study, gold catalysts were also applied in direct oxidative esterification of primary alcohols or aldehydes with methanol to methyl esters.[58,65] Inspired by these reports, we studied benzyl alcohol oxidation with Au/Al_2O_3 in methanol and other aliphatic alcohols. In the previous studies, small amount of sodium methoxide was used to increase the selectivity towards the methyl ester. Instead, 5 mol% NaOH was applied to give full conversion and very high selectivity (96%) to methyl benzoate in 1 h. With higher alcohols (ethanol, isopropanol and cyclohexanol) considerably longer reaction times were required to reach reasonable conversions, and high selectivity was achieved only in ethanol.

Our results elucidate the tunable chemoselectivity of gold catalysis and the importance of reaction media. While usually a catalyst is optimized for one product, a “one for all” catalytic systemwas developed here; using one catalyst in different reaction conditions to selectively switch from one reaction product to another (Scheme 15).



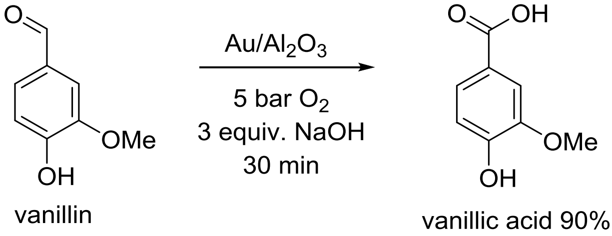
Scheme 15 Solvent-controlled oxidation of benzyl alcohol with Au/Al_2O_3.[I]

4.4 Oxidation of vanillin[IV]

Inspired by the studies on benzyl alcohol oxidation, we turned to a related compound, vanillin (4-hydroxy-3-methoxybenzaldehyde). Vanillin is one of the few high-value chemicals commercially produced from lignin and its oxidation product vanillic acid is used in food, pharmaceutical and chemical industries.[111] Being an aldehyde, vanillin should be easier to oxidize than the corresponding alcohol, but relatively few reports were found on vanillin oxidation.[112]

The Au/Al_2O_3-DIE described in Publication II was chosen as catalyst and two additional catalysts, Au/Al_2O_3-DPU and Au/TiO_2, were prepared. According to our previous results, additional base is required in oxidation of aldehydes to acids.[I] With this in mind, the studies on vanillin oxidation were iniated with 1 equiv. NaOH, which was optimal in benzyl alcohol oxidation. However, only low conversion and moderate selectivity were obtained with Au/Al_2O_3-DPU in 2 h reaction. Increasing the amount of base to 2 equiv. gave a surprising result; selectivity increased to 99% and 79% conversion was already achieved in 30 min. Further increases of the amount of base increased the conversion to over 90% without affecting selectivity (Scheme 16). Turn-over frequencies up to 1300 h^{-1} were measured with Au/Al_2O_3-

DPU. Similarly, very high selectivities were obtained with Au/Al_2O_3-DIE and Au/TiO_2 when at least 2 equiv. NaOH was used.



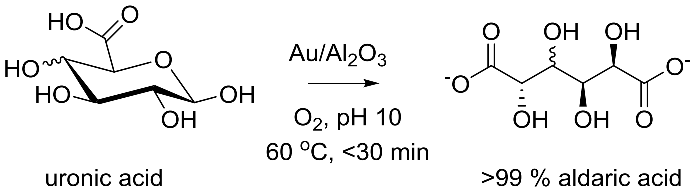
Scheme 16 Oxidation of vanillin using gold catalysts.[IV]

Evidently, the additional base prevents side reactions as well as catalyst deactivation. As 1 equiv. NaOH would be sufficient to deprotonate the produced acid, we presumed that the acidic phenolic hydroxyl could affect the catalyst deactivation and side reactions. Further studies were carried out using sodium carbonate and sodium bicarbonate, both weaker bases than hydroxide. Selectivities obtained with NaOH or Na_2CO_3 were similar, whereas $NaHCO_3$ gave lower selectivity regardless of the amount used. However, high conversion was obtained only using at least 2 equiv. hydroxide, a strong base. Vanillin is known to undergo autocatalytic degradation to quinonic compounds under mildly alkaline conditions,[113] which might account for the decreased selectivity observed herein. This study represents the first description of heterogeneous gold catalysts in selective oxidation of vanillin.

4.5 Oxidation of carbohydrates in alkaline conditions[II]

The aldehyde group of monosaccharides is efficiently oxidized to aldonic acids using supported gold catalysts in alkaline conditions (Section 3.2).[85] Aldaric acids, diacids of sugars, are also important building block chemicals.[11] Having the high selectivities of gold catalysts in mind, we attempted to oxidize both the aldehyde and the primary hydroxyl group of glucose to obtain glucaric acid, the corresponding diacid. However, oxidation of the primary hydroxyl group requires severe conditions; our attempts to use pressurized oxygen and excess base resulted in product degradation and low selectivity.

In the case of uronic acids, components of e.g. hemicelluloses and pectin, the primary hydroxyl is already oxidized by nature.[84] Similarly to aldoses, uronic acids are sensitive towards degradation and isomerization in highly alkaline media.[114] Therefore, the oxidation experiments were carried out using an automatic titrator to maintain constant pH and to avoid the use of excess base. With dioxygen as oxidant, mass transfer limitations due to the low solubility of oxygen were prevented by optimizing catalyst amount to 0.09 mol% Au/Al_2O_3. Quantitative oxidation of D-glucuronic acid to glucaric acid was achieved at pH 10 and 60 °C in only 30 min. Similarly, the isomeric D-galacturonic acid was oxidized quantitatively into galactaric acid (Scheme 17). The controlled continuous addition of base was clearly favourable in terms of selectivity; no isomerization, degradation or side reactions were observed.



Scheme 17 Oxidation of glucuronic and galacturonic acid with Au/Al_2O_3-DIE.[II]

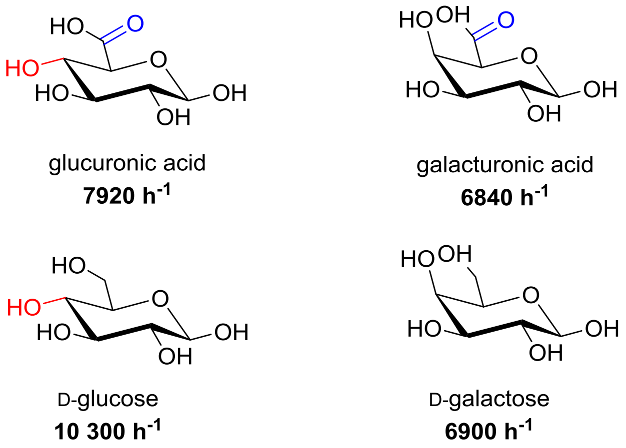
Quantitative conversion of glucuronic acid was achieved also at pH 8-9, even though the oxidation activity decreased considerably (Table 9). At pH 8, the initial oxidation rate started decreasing after ca. 40% conversion indicating catalyst deactivation. At low pH, the produced acid is not completely neutralized and a small part of the carboxylic acid groups are protonated. The free acids can adsorb on the catalyst surface, consequently blocking the active sites.[73] In alkaline medium however, the acids are deprotonated and readily desorb the catalyst surface; at pH 9-10 the initial oxidation rate was maintained until 85% conversion rate was achieved.

In further studies, reaction temperature was shown to have a stronger effect on the oxidation at pH 8 compared to pH 9-10. Accordingly, the apparent activation energy E_a, derived from the Arrhenius plot, was considerably higher at pH 8 compared to pH 9-10 (Table 9). In heterogeneous catalysis, the apparent activation energy observed is in fact the activation energy of the reaction modified by heat of adsorption ΔH_{ad} of the reaction species.[115] At pH 8, the acids are not completely deprotonated and the energy required for desorption is higher compared to more alkaline pH. While the E_a values obtained are comparable to those reported previously in aldose oxidation,[40,41] the effect of pH has not been previously addressed.

Table 9 Effect of pH on activity and apparent activation energy $\boldsymbol{E_a}$ in glucuronic acid oxidation with Au/Al_2O_3-DIE.[II]

pH	TOF (h^{-1})	E_a (kJ/mol)
10	7920	24.6
9	5970	26.5
8	3250	45.3

The influence of the carbohydrate structure on catalysis was studied by comparing the oxidation of glucuronic and galacturonic acid to their corresponding hexoses, D-glucose and D-galactose. With varying activities, all of the substrates were quantitatively converted to the corresponding aldaric or aldonic acids (Scheme 18). Axial hydroxyl at C_4 (galactose vs. glucose) and carboxylate at C_6 (glucuronic acid vs. glucose) had a similar rate-decreasing effect on the oxidation. Unexpectedly, these effects are not cumulative; galacturonic acid, although having both axial hydroxyl at C_4 and carboxylate at C_6, oxidized as easily as galactose or glucuronic acid.



Scheme 18 Turn-over frequencies in oxidation of uronic acid and aldoses with Au/Al_2O_3-DIE at pH 10 and 60 °C.

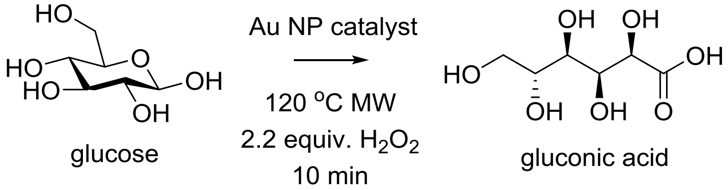
In parallel with this work, oxidation of uronic acids with gold catalysts was developed by van der Klis *et al.*[116] With Au/TiO_2 and 1 equiv. NaOH added at the beginning of the reaction, galacturonic acid was oxidized with 97% yield in 3 h reaction. Surprisingly, glucuronic acid was oxidized with only 85% yield in 5 h under otherwise similar conditions. As shown in our work, the controlled continuous addition of base provides substantial improvement; quantitative conversions for both uronic acids are achieved with very high activities.[II]

4.6 Base-free oxidation of glucose[III]

Most of the research on oxidation of carbohydrates has focused on alkaline conditions, because under acidic conditions noble metal catalysts have suffered from deactivation and slow oxidation rates.[117] However, as described in Section 3.2.3, there is growing interest in base-free oxidation of glucose to gluconic acid. Inspired by this, we started studies on base-free glucose oxidation with gold catalysts using pressurized oxygen. However, the reaction resulted only in low conversions and catalyst deactivation.

To promote oxidation, microwave assisted heating was introduced, which has been applied in our laboratory in several studies. Hydrogen peroxide was applied as alternative oxidant, since the use of pressurized oxygen in closed microwave vials was inapplicable with this system. Gold catalysts with different support materials were selected, including MgO, $MgAl_2O_4$ and Al_2O_3, as the catalyst support can have a strong effect on the H_2O_2 decomposition rate.[94] Both Au/$MgAl_2O_4$ and Au/Al_2O_3-DIE oxidized glucose with high selectivity to gluconic acid (Table 10). The highest activity was observed with Au/Al_2O_3; yields up to 76% were achieved in only a 10 min reaction. However, in the case of Au/MgO, the support was completely dissolved in the acidic media during the reaction.

Table 10 Microwave-assisted base-free oxidation of glucose to gluconic acid with gold catalysts.[III]



Entry	Catalyst	Glc:Au	Conv. (%)	Select. (%)	TOF (h^{-1})
1	Au/$MgAl_2O_4$	870	54	93	10 400
2	Au/Al_2O_3-DIE	1110	83	87	12 900

Both the high reaction temperature and microwave heating were crucial for high conversion. Comparison of oil bath heating to MW under otherwise similar conditions confirmed the efficiency of microwave heating; significantly higher conversions were achieved with MW, while selectivities were similar with both methods. Secondary reactions and product degradation decreased the selectivity slightly. The main byproducts were keto-gluconic acids and 4-5 carbon atom aldonic and aldaric acids, based on GC/MS analyses. Similar selectivities were previously reported under acidic conditions at considerably lower temperatures and longer reaction times.[77]

Previous studies by Saliger *et al.* showed that the effective oxidizing agent is not hydrogen peroxide itself, but forms by its decomposition on the gold catalyst.[76] By studying the rate of oxygen generation from H_2O_2, we showed that the oxidation activity of the catalysts was clearly associated with their ability to decompose H_2O_2. Of the two catalysts, Au/Al_2O_3-DIE showed considerably higher activity and stability in the decomposition of H_2O_2, corresponding with the results in glucose oxidation.

The use of microwave irradiation to promote chemical reactions is increasing rapidly,[118] though reports on microwave-assisted reactions using gold catalysts are still rare.[119] In this work, we have shown that microwave heating is a valuable tool for gold-catalysed glucose oxidation enabling shortened reaction time and high selectivity; a very fast and efficient method compared to those reported previously.

4.7 Catalyst reusability[II, III]

Reusability of the gold catalysts was studied by recycling experiments in both alkaline[II] and base-free[III] carbohydrate oxidation. Characterization of the recycled catalysts elucidated the effect of reaction conditions on the catalyst properties. Common causes for catalyst deactivation are particle sintering, metal leaching and poisoning or adsorption of organic species on the catalyst surface, which were studied by TEM, AAS and TGA, respectively.

In the case of glucuronic acid oxidation with Au/Al_2O_3, the selectivity of the catalyst was maintained, while the activity dropped 35% in a successive reaction.[II] The decreased activity was attributed to reduced Au surface area due to aggregation and coalescence of gold nanoparticles, clearly detected by TEM (Figure 1). The size of the aggregates ranged from 6.0 to 9.5 nm, while some smaller particles were also present.

a) b)

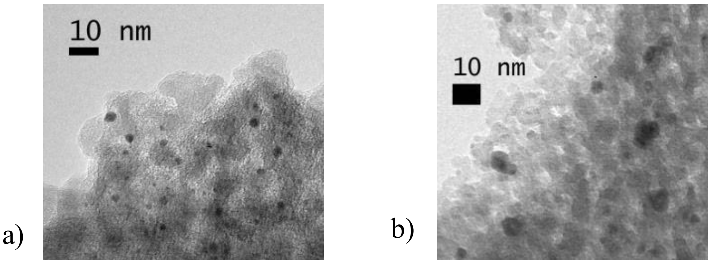


Figure 1 TEM images of Au/Al_2O_3-DIE a) fresh and b) after oxidation of glucuronic acid.[II] Published by The Royal Society of Chemistry.

Acidic conditions are especially demanding for gold catalysts, as described in Section 3.2.3. In microwave-assisted base-free oxidation of glucose, the Au/$MgAl_2O_4$ catalyst lost over 30% of its activity in a successive reaction.[III] According to TEM analysis, the mean particle size of Au/$MgAl_2O_4$ increased from 3.8 nm to 4.4 nm, which is the likely cause of the deactivation. In addition, the mean particle size of Au/Al_2O_3 increased from 2.4 nm to 3.6 nm after two runs, which is in accordance with previous observations of Au NPs sintering under acidic conditions.[77] Nevertheless, the Au/Al_2O_3 catalyst maintained both activity and selectivity upon recycling; no deactivation was detected in four consecutive runs at 100 °C. This was the first report on recycling of gold catalyst in acidic conditions without the need for catalyst regeneration.

5 Conclusions

The discovery of the catalytic properties of gold has advanced the field of selective oxidation significantly. Using gold nanoparticle catalysts, environmentally benign oxidation of alcohols and aldehydes is achieved under mild conditions with oxygen or hydrogen peroxide as oxidant. Gold catalysts have shown very high selectivities, extreme activities and high stability, often surpassing other metal catalysts. Especially, gold catalysts are attracting a great deal of interest in selective transformations of biomass-derived compounds, such as oxidation of glycerol and carbohydrates. Efficient valorization of biomass requires the development of novel green processes suitable for the highly functionalized substrates. Due to their unique properties, gold catalysts are promising catalysts for these applications.

In this work, gold catalysts were studied in selective oxidation of alcohols, aldehydes and carbohydrates. Using benzyl alcohol as a model compound, the effect of reaction media on the chemoselectivity of the oxidation was clarified. Based on the results, the concept of "one for all" catalytic system was developed, allowing the selective production of aldehyde, acid or ester with a single catalyst. These results inspired the author to study the oxidation of vanillin, an aromatic aldehyde available from lignin. The selectivity of the oxidation showed an interesting dependence on the amount of added alkali, and as a result, very high selectivity to vanillic acid was achieved for the first time with gold catalysts.

Gold-catalysed oxidation of carbohydrates to sugar acids has been extensively studied in alkaline conditions. In this work, the substrate scope was extended to uronic acids, allowing highly selective production of aldaric acids, or sugar diacids. Comparison of uronic acid oxidation to the corresponding aldoses elucidated the effect of substrate structure on the oxidation rate. Moreover, apparent activation energy of the oxidation was shown to depend on pH of the reaction solution, showing the strong influence of the added base on gold catalysts.

There is growing interest in base-free oxidations, but acidic conditions are demanding for gold catalysts, as deactivation and slow oxidation rates have been observed. A very efficient method for base-free oxidation of glucose, utilizing microwave irradiation, was developed in this work. Significantly shortened reaction times and very high activities compared to previous reports were achieved with hydrogen peroxide as green oxidant. The oxidation activity of the catalysts was correlated to their ability to decompose hydrogen peroxide. Furthermore, activity of the Au/Al_2O_3 catalyst remained constant in four consecutive runs, demonstrating for the first time the recycling of gold catalyst in acidic conditions without the need for catalyst regeneration.

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