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Catalysis Today 57 (2000) 127–141

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Selective oxidation of alcohols and aldehydes on metal catalysts

Michèle Besson *, Pierre Gallezot

Institut de Recherches sur la Catalyse-CNRS, 2 Avenue Albert Einstein, 69626 Villeurbanne Cédex, France

Abstract

Oxidation of aldehydes, alcohols or carbohydrate derivatives can be performed with air in aqueous media, in the presence of palladium and platinum catalysts under mild conditions (293–353 K and atmospheric pressure). These reactions provide valuable products and intermediates for fine chemistry. They have been known for a long time, but much effort in the last 20 years has focused on this approach, because these catalytic reactions are environmentally friendly and could replace stoichiometric oxidations with mineral oxidizing agents. An oxidative dehydrogenation mechanism on the reduced metal surface has been generally accepted. During this process, a strong deactivation of the catalysts is often reported, which is a cause of serious concern for process development. Several causes of deactivation have been put forward: oxidation of metal, blocking of active sites by strong adsorption of side-products, metal leaching and growth of platinum crystallites. The addition of certain p-electron metal promoters (e.g. Bi, Pb) has been shown to play a useful dual role in reducing catalysts deactivation and in changing the selectivity of reactions. The performances of the catalysts can also be improved by modification of the metallic surface with strongly adsorbing nitrogen-containing bases or phosphines.

A few illustrative examples will be given, which show that carbohydrates, aliphatic or aromatic alcohols, and polyols can be oxidized with high selectivities into valuable products.

Keywords: Oxidation; Alcohols; Aldehydes; Metal catalysts

1. Introduction

This review deals with the liquid phase oxidation, with molecular oxygen, of alcohols, aldehydes, and carbohydrates in the presence of platinum or palladium metal catalysts. These catalytic reactions proceed under mild conditions (293–353 K and atmospheric pressure) and are attractive for the preparation of fine chemicals. They operate via an oxidative dehydrogenation mechanism whereby the functional groups adsorb and dehydrogenate on the metal surface, followed by oxidation of the adsorbed hydrogen atoms. Early, Heyns et al. [1,2,106] proposed a reactivity scale for the oxidation of the different functional groups on Pt/C catalysts. This field of research matured over the last 20 years following a series of studies by groups at Eindhoven [3–24], Delft [25–39], Zürich [40–56], and Villeurbanne [57–67], while the oxidation of glycerol and derivatives was thoroughly studied by Kimura [68–73]. A few review papers have been published on the liquid phase of alcohols and carbohydrates on metal catalysts [31,48,74–76].

In a first part, the general features of oxidation reactions on metal catalysts will be described. Then, recent studies reporting high selectivity achievements or process innovation will be examined in more details.

2. General features of liquid phase oxidation on metal catalysts

2.1. Reaction mechanism

It was suggested, at a very early stage [1,2], that liquid phase oxidation reactions of alcohols on

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* Corresponding author.

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PII: S0920-5861(99)00315-6

metal surfaces proceed via a dehydrogenation mechanism followed by the oxidation of the adsorbed hydrogen atom with dissociatively adsorbed oxygen. This was supported by kinetic modeling of oxidation experiments [3], and by direct observation of hydrogen evolving from aldose aqueous solutions at basic pH (>11) in the presence of platinum or rhodium catalysts [25]. The dehydrogenation mechanism was also supported by various physical and chemical measurements. Thus, oxidation experiments of ethanol or 2-propanol conducted with ^{18}O-labeled oxygen showed that this isotope was not incorporated into reaction products [77]. Measurements of electrode potential showed that the potential of the platinum catalysts in alcohol solutions was almost similar to that of the hydrogen electrode, i.e. Pt-surface partly covered by adsorbed hydrogen [78]. Similar measurements during oxidation of 2-propanol demonstrated that the Pt-surface was predominantly covered with hydrogen even though the oxidation reaction was run under 1 bar of oxygen [79].

A number of different formalisms have been proposed to describe the surface chemistry of the oxidative dehydrogenation mechanism. For the dehydrogenation of reducing sugars in basic solutions, it was suggested [25] that the unprotected aldoses in ionized form adsorb on the metal surface, and transfer a hydrogen from the C_1 carbon atom to the metal; the resulting lactone is then converted into the corresponding carboxylate in basic medium.

Because oxidation reactions can also be conducted in neutral or slightly acidic media, where deprotonation of the OH group is unlikely, a dehydrogenation pathway occurring entirely on the metal surface was also proposed [26,28,31]

$$\mathrm{RCH_2OH_{sol}} \leftrightharpoons \mathrm{RCH_2OH_{ads}} \rightarrow \mathrm{RCHO_{ads}} + 2\mathrm{H_{ads}} \quad (1)$$

The surface reaction should involve a first dehydrogenation giving the alkoxide $\mathrm{RCH_2O_{ads}}$, which is subsequently dehydrogenated into the corresponding aldehyde. The second step is more demanding, as demonstrated by experiments showing a strong isotope effect in the rate of oxidation of α-deuterated and non-deuterated 2-propanol [79]. Adsorbed hydrogen atoms are removed from the surface by reaction with oxygen dissociatively adsorbed on the metal.

If water is present in the reaction medium, aldehydes may hydrate to form a geminal diol, which dehydrogenates to form the corresponding acid

$$\begin{aligned} &\mathrm{RCHO_{sol}} + \mathrm{H_2O_{sol}} \\ &\quad \leftrightharpoons (\mathrm{RCH(OH)_2})_{\mathrm{sol}} \leftrightharpoons (\mathrm{RCH(OH)_2})_{\mathrm{ads}} \\ &\quad \rightarrow (\mathrm{RCOOH})_{\mathrm{ads}} + 2\mathrm{H_{ads}} \qquad (2) \end{aligned}$$

The aldehyde formed transiently is usually not detected in the reaction medium. However, in 5-hydroxymethylfurfural oxidation [28], the aldehyde intermediate was formed with a high selectivity. This was attributed to the fact that the geminal diol did not form easily due to a conjugation of the carbonyl group with the aromatic furan nucleus. Also a good selectivity was obtained in the case of cinnamyl alcohol oxidation to cinnamyl aldehyde, because there was a negligible hydration of the C=O group of the aldehyde conjugated with C=C bond and aromatic nucleus [45,50]. In the presence of organic solvents, alcohol oxidation stops at the aldehyde stage because the geminal diol could not form; however, this is of limited practical importance because for safety reason most of the organic solvents could not be used in the presence of oxygen and metal catalysts.

Another oxidation pathway, involving the reaction of the organic substrate with oxygen, both adsorbed on the metal surface, has been proposed by the Eindhoven group [15,19]. Thus, in a study based on the kinetic modeling of the ethanol oxidation on platinum, Van den Tillaart et al. [19] proposed that, following the first step of abstraction of the hydroxyl hydrogen of ethanol, the ethoxide species $\mathrm{CH_3CH_2O_{ads}}$ did not dehydrogenate further, but reacted with dissociatively adsorbed oxygen

$$\mathrm{CH_3CH_2OH} \rightarrow \mathrm{CH_3CH_2O_{ads}} + \mathrm{H_{ads}} \qquad (3)$$

$$\mathrm{CH_3CH_2O_{ads}} + \mathrm{O_{ads}} \rightarrow \mathrm{CH_3CHO} + \mathrm{OH_{ads}} \qquad (4)$$

$$\mathrm{H_{ads}} + \mathrm{OH_{ads}} \rightarrow \mathrm{H_2O} \qquad (5)$$

In conclusion, the oxidative dehydrogenation mechanism is widely accepted, but the precise reaction pathway will be still under debate for some time because the nature and concentration of adsorbed species are not known.

2.2. Catalyst deactivation

Oxidation catalysts based on platinum metals could undergo irreversible deactivation due to the modification of the catalyst structure (metal sintering or leaching), or reversible deactivation due to poisoning of the metal surface by strongly adsorbed species (oxygen, impurities, products, or by-products).

2.2.1. Irreversible deactivation due to modification of catalyst structure

The metal dispersion in Pt/C catalysts during glyoxal oxidation [57,58], and in Pd/C catalysts during glucose oxidation [59,60] was hardly changed after reaction. These catalysts were prepared by ion exchange of acidic groups on carbon, which resulted in very stable metal dispersion because of the interaction of the particles with functional groups of the support. Schuurman et al. [17] reported a moderate sintering of platinum catalysts from 2.2 to 3.2 nm in methyl-α-glucoside oxidation. In a recent reinvestigation of this reaction [23], it was concluded that there was almost no growth of platinum particles on a Pt/graphite prepared by ion exchange under oxidizing condition. However, treatment with hydrogen at high pH destroying the functional groups, and the interaction of the platinum particles with the graphite support, enhanced particle growth. In a study of L-sorbose oxidation, Bakos et al. [55] observed by STM the corrosion and restructuring of large platinum particles prepared by electrodeposition. Metal leaching, particularly of electropositive metal promoters should be of serious concern, especially when large amounts of these promoters are used; unfortunately, this point was not well documented in the literature. It was reported [32] that both platinum and aluminum from Pt/Al_2O_3 catalysts leached away in the aqueous solutions of D-ribose and D-xylose; platinum leaching was much larger for D-ribose because the configuration of this carbohydrate was more favorable for metal complexation. No leaching of platinum or bismuth from Pd–Bi/C catalysts was observed in glucose oxidation carried out on basic pH [60], nor from Pt–Bi/C catalysts employed in the oxidation of glycerol to dihydroxyacetone even at slightly acidic pH [61]. Bismuth was detected in solutions in the course of oxidation of tartronic to mesoxalic acid on Pt–Bi/C catalysts under acidic conditions [66]; however, this is one of the most unfavorable case, because of the high chelating properties of the reactants and products, and low value of the pH (1–2). Mallat et al. [80] showed, by measurements of dissolution potentials, that lead adatoms on the surface of platinum or palladium are much more stable to anodic oxidation than bulk lead. Brönnimann et al. [53] showed by XPS and ICP–AES measurements that there was a loss of platinum and bismuth after oxidation of L-sorbose on Pt–Bi/Al_2O_3 catalyst; this might be due primarily to the instability of alumina in the reaction medium. Loss of palladium in Pd/$CaCO_3$ during oxidation of 2-methylphenoxyethanol [81] could also be attributed to the instability of calcium carbonate in solution. Schuurman et al. [17] and Vleeming et al. [23] observed a change in the morphology of Pt particles on graphite but did not measure any platinum leaching in solution.

To conclude this section, transport phenomena of platinum atoms assisted by strong chelating molecules have been clearly demonstrated, particularly on large particles not well anchored on supports. Cases of leaching of platinum in solution evidenced by ICP–AES analysis have been reported mainly for catalysts on alumina support, which is also more liable to leach than carbons. Bismuth promoter is liable to leach particularly in the presence of chelating agents at acidic pH.

2.2.2. Deactivation due to adsorbed species

Metal catalysts could be deactivated by blockage of the surface by strongly adsorbed molecules either impurities or reaction products remaining adsorbed on the surface, or adsorbed oxygen. The later effect known as “over-oxidation” or “oxygen poisoning” of the surface is well documented, and of great practical importance in liquid oxidation on metals.

Mallat et al. [42,43,45–48,50] have studied extensively the process of deactivation of metal catalysts by impurities, by-products or reaction products, which was named “chemical deactivation” or “self-poisoning”. Side products consisting of polymeric carbonyl species were detected by chromatographic and spectroscopic methods in the oxidation of 1-methoxy-2-propanol with air and these species were identified as the primary cause of deactivation. Since chemical deactivation favors further deactivation by over-oxidation, they suggested that a simple method to distinguish the two deactivation processes was to investigate the response of the system to a change in the relative rate of oxygen supply. Thus, if deactivation could be eliminated by increasing the reaction rate (e.g. by working at higher temperatures) or by changing temporarily the air flow to nitrogen, deactivation by side products was unlikely. However, in most cases the distinction between the two types of surface poisoning was not unambiguous. Poisoning by irreversibly adsorbed side-products was also invoked in the case of cinnamyl alcohol oxidation [45] and in 1-phenyl-ethanol oxidation [44]. In the latter investigation, the poisoning was attributed to the dissociative adsorption of the alcohol leading to irreversibly adsorbed species.

The deactivation of liquid phase oxidation reactions by over-oxidation of the metal surface has been a subject of great importance. The dynamical balance of competitive adsorption of organic substrate and oxygen controls the initial reaction rate and the equilibrium tends to shift towards predominant oxygen coverage as the substrate concentration decreases.

The activity was usually regenerated by flowing nitrogen instead of air, but the activity was less and less regenerated in successive cycles of reaction alternating flow of air and nitrogen. Because of the progressive loss of reactivation efficiency, it was suggested that oxygen atoms penetrate more and more deeply in the subsurface or in platinum bulk [13]. Depending upon the starting procedure (platinum surface reduced or oxidized to different extent), upon reaction conditions (ethanol concentration, partial oxygen pressure), different steady states for the oxidation of ethanol on platinum have been measured [21].

The structure of the oxygen-covered surface was the subject of few studies. Recent in situ EXAFS experiments on platinum particles during cyclohexanol oxidation, showed that the platinum surface in the deactivated state was not entirely oxidized since the Pt–O distances lies between those observed for adsorption of cyclohexanol on metal (2.1 Å) and those of platinum oxide (2.06 Å) [24]. The lowest degree of oxidation was found after a reductive startup whereas the oxidative startup with the lowest reactant concentration resulted in an almost completely oxidized platinum surface.

Various factors account for the deactivation of metal by over-oxidation, namely:

Effect of catalyst structure and texture: (a) Metals with a higher oxidation potential will be less prone to oxidation [29,57]. Thus, among Pt-group metals, platinum is the less easily poisoned by over-oxidation, followed by palladium. (b) Small metal particles deactivate more readily than larger ones. This was observed in the oxidation of 2-propanol [81] on platinum catalysts and D-glucose oxidation on Pd/C catalysts where the deactivation was attributed to the stronger affinity of oxygen for the particles smaller than 2 nm [59]. The effect of particle size was less marked in the oxidation of methyl-α-D-glucoside on Pt-particles supported on graphite [22]. (c) Vleeming et al. [22] found that the turnover of methyl-α-D-glucoside oxidation was 3.7 times higher on platinum supported on carbon fibrils than on graphite; this was attributed to the higher hydrophilic character of the carbon fibrils which were oxidized by HNO_3 treatment. (d) According to van Dam et al. [27], mass transfer limitation in pores may be used to limit the deactivation provided the metal particles are uniformly distributed in extruded supports. Because the concentration of oxygen decreases continuously from the edge to the core of the extrudate, there is always a zone at a certain depth from the external surface where the concentration of oxygen is sufficiently high to feed the oxidation reaction, but sufficiently low to avoid metal over-oxidation.

Effect of the nature of the organic substrate: (a) Organic substrate has a high affinity for the metal, oxygen will not prevent its adsorption. Thus, the absence of poisoning in the oxidation of 5-hydroxymethylfurfural on various platinum-group metals was attributed to the strong bonding of the substrate via the π-electrons of the furan ring [28]. (b) The higher the reduction potential of the substrate, the higher the catalyst will be maintained in a reduced state and the lower will be the deactivation. Thus, platinum catalysts did not deactivate for the oxidation of strong reducing agent like glyoxal [57,58]. The deactivation should be lower for an aldehyde than for a primary alcohol, which accounts for more severe deactivation problems in the case of gluconate or methyl-α-D-glucoside than for D-glucose.

Factors depending on the reaction conditions: Lower initial reaction rates and higher deactivation were observed for reactions run at acidic pH (e.g. oxidation of D-glucose to D-gluconic acid [33,35], and oxidation of glycerol to glyceric acid [61]), because carboxylic acids formed remain strongly adsorbed on metals surface. The higher the oxygen pressure in the liquid phase, the greater the risk of over-oxidation. If the initial rate of oxidation is fast enough, oxygen dissolved in solutions will be totally consumed by reacting with the organic molecule on the metal surface; the reaction rate is then limited by gas–liquid oxygen mass transfer and the risk of over-oxidation of the metal is weak. For sluggish reaction, over-oxidation can be prevented by conducting the reaction at low concentration of oxygen, either by dilution with nitrogen, or by taking advantage of mass transfer limitation in the catalyst pores [27]. Measurement of the electrochemical potential of the catalyst was found to be a reliable parameter to monitor the oxidation state of the surface and thus could be used to regulate the rate of oxygen supply to the catalyst [43,51].

To conclude, it should be stressed that “chemical deactivation” (or “self-poisoning”) and “over-oxidation” are not mutually exclusive. On the contrary, they should result in a synergetic poisoning since any blockage of surface sites by impurities or side products would decrease the rate of reaction and therefore the consumption of oxygen, thus favoring the over-oxidation of the surface.

2.3. *Role of metal promoters*

Metal promoters, mainly lead and bismuth, were used extensively to improve the rate and selectivity of platinum and palladium catalysts. There are numerous reports on the beneficial effect of bismuth or lead promoters on the rate of oxidation reactions [14,40,41,50,54,60,62,67,97]. Thus, the initial rate of cinnamyl alcohol oxidation was 26 times higher on a Pt–Bi/Al_2O_3 catalyst ($Bi/Pt_S = 0.5$) with respect to unpromoted catalysts [50]. Similarly, the rate of glucose oxidation to gluconate was 20 times higher on Pd–Bi/C catalysts ($Bi/Pd_S = 0.1$) than on Pd/C. The presence of bismuth increased the rate of oxidation of 9-decen-1-al to 9-decenoic acid [67] (see Section 3.3).

Different interpretations were given for the promoter effect on reaction rate. According to Mallat et al. [41,42], the main course of catalyst deactivation during oxidation of secondary alcohols is the formation and strong irreversible adsorption of by-products (e.g. aldol-dimerization of the carbonyl compound). The presence of bismuth or lead on the surface of platinum decreases the size of active site ensembles, thus suppressing the poison formation [43]. It was also proposed that the geometry of active site ensembles depends upon the size of the metal promoter [47]. Thus the higher is the number of active sites which the promotor occupies, the higher is its promoting effect ($Ag < Sn$, $Pb < Bi$). Another interpretation, also given by Mallat et al. [47], was that bismuth adatoms adsorb oxygen to form Pt–Bi–OH species on the surface, which act as new active site for the oxidation of alcohol adsorbed on platinum. According to Besson et al. [60], because of its higher affinity for oxygen, bismuth acts as a co-catalyst protecting palladium from over-oxidation according to the scheme in Fig. 1.

In addition to their beneficial effect on the rate of oxidation, bismuth and lead favor the oxidation of polyhydroxy carboxylic acids to their α-keto derivatives. Thus, in an early study Smits et al. [10,11]

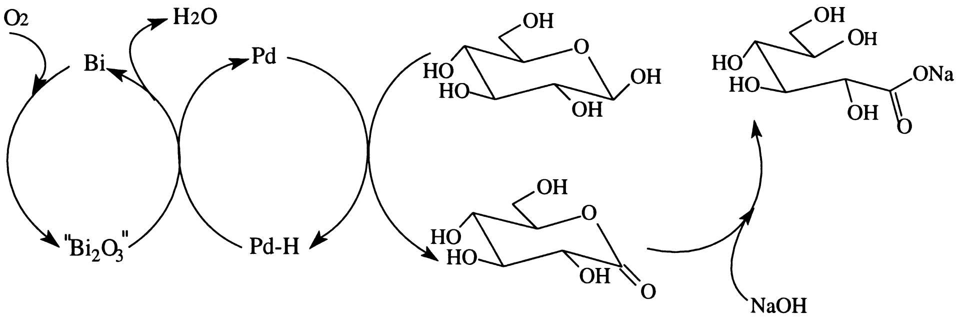

Fig. 1. Proposed mechanism of glucose oxidation on Pd–Bi catalyst [60].

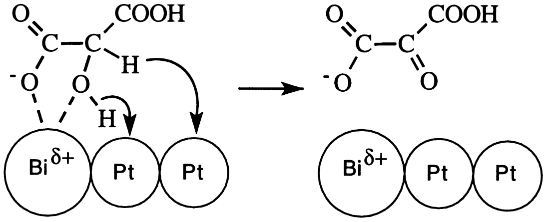

Fig. 2. Proposed complexing mechanism for selective catalytic oxidation of the secondary hydroxy function of tartronic acid [66].

showed that in D-gluconate oxidation, the selectivity to 2-keto-D-gluconate was improved by the addition of lead promoter deposited on Pt/C catalysts. It was suggested that gluconate molecules were complexed by the lead atoms via the oxygen atoms of the carboxyl group and of the α-hydroxyl group. A similar effect was reported by Besson et al. [63].

Abbadi and van Bekkum took advantage of this particular promoting effect to tune the selectivity of platinum with bismuth and lead for the oxidation of α-hydroxy acids to α-ketonic acids. Thus, 2-keto-aldonic acids [34], β-hydroxypyruvic acid [36], and 2-keto-lactobionic acid [37] were obtained with a high selectivity (see Section 3.1). Similarly, Pt–Bi catalysts were employed to obtain dihydroxy acetone from glycerol [61,69,70], hydroxypyruvic acid from glyceric acid [62], and mesoxalic acid from tartronic acid [66] (see Section 3.2). The mechanism of bismuth promotion, given in the scheme in Fig. 2 was similar to those proposed earlier for the oxidation of α-hydroxy acids to α-ketonic acids [10,11].

In the case of furfural oxidation on Pt/C catalyst, Verdeger et al. [82] interpreted the beneficial effect of lead on the activity and selectivity to furoic acid by the π-adsorption of the furfural ring on the promoter atoms deposited on the platinum surface.

Gold has been used as a promoter of a platinum catalyst for the oxidation of gluconic acid to glucaric acid [63]. Even a very small addition of gold (Au/Pt molar ratio = 0.03) produced a significant improvement of reaction rate with respect to the parent catalyst. The promoter effect, which was particularly noticeable at high conversion, can be accounted for by a decrease in the poisoning of the metal surface, either by oxygen or by acidic by-products. Unlike bismuth, gold did not increase the selectivity in 2-ketogluconate.

2.4. *Role of organic modifiers*

The group of Mallat and Baiker [46,49,52–54] employed tetraalkylammonium hydroxides, tertiary amines and phoshines as additives to improve the activity and selectivity of platinum catalysts in L-sorbose oxidation to 2-keto-L-gulonic acid (2-KLG, see Section 2.2.7). Rate acceleration was attributed to a beneficial effect of the amine on the hydration of the intermediate aldehyde. The best selectivity enhancement was obtained with hexamethylenetetramine (HMTA) and was attributed to a preferential adsorption of the sorbose molecule via the hydroxyl group on C-1, because of the formation and steric arrangement of a complex between HMTA and L-sorbose via hydrogen bonding [52]. In the same way, Heinen et al. [38] improved the selectivity to 2-keto-D-gluconic acid in D-fructose oxidation by using small amounts of HMTA to modify the surface of Pt/C catalysts.

2.5. *Reactors and reaction conditions*

Oxidation reactions on metals were usually carried out in batch reactors containing the solution of the organic substrate to be oxidized and a suspension of the catalyst in powder form. Typically, reactions were run at atmospheric pressure under continuous stirring with air bubbling through the suspension maintained at constant temperature in the range 20–80°C. Oxidation reactions were carried out with pH ranging from 2 to 13, but in many instances from 7 to 9. The pH was regulated by the addition of dilute alkali solutions under the control of a pH regulator. Oxygen electrodes were also used to monitor the oxygen pressure in the liquid phase which was very useful to control whether the reaction kinetics was limited by gas–liquid oxygen mass transfer (see, e.g. [60]) or to control the rate of oxygen supply (see, e.g. [29]). A platinum electrode associated with a reference electrode was used to measure the electrochemical potential of the catalyst providing in situ information on the oxidation state of the active metal surface, which may be used to optimize the oxygen supply to the reaction medium (see, e.g. [51]). The reaction kinetics was followed by monitoring the addition of alkali solution required to maintain a constant pH, or in a more reliable way, by chromatographic analysis of the reaction medium taken at periodic time intervals.

Reactions were also carried out in stirred slurry reactor operating in continuous mode with the solution injected with a pump and the catalyst retained by a filter at the liquid outlet [19,21]. A trickle-bed reactor was used for glycerol oxidation [64], but the selectivity was lower than in batch reactor except at small conversion. A fixed-bed reactor was also used by Kimura [70,71,73] for the oxidation of glycerol and derivatives.

Most of liquid phase oxidation reactions were carried out in water, sometimes on highly concentrated solutions, e.g. for glucose up to $1.7\,\mathrm{mol\,l^{-1}}$ [60]. For water insoluble alcohols, organic solvent could in principle be used but most of them should be strictly avoided for safety reason. However, acetic acid was used as solvent in the case of retinol oxidation to retinal [83]. Oxidations of insoluble molecules were also performed in the presence of surfactants. Thus Mallat et al. [50] oxidized cinnamyl alcohol (3.5 g) with Pt–Bi catalysts (0.14 g) suspended in water (30 ml) in the presence of dodecylbenzene sulfonate (0.14 g) and Li_2CO_3 (0.14 g). The excellent selectivity to cinnamyl aldehyde (96% at 83% conversion) was attributed to the negligible hydration of the aldehyde because of the conjugation of C=O, C=C and aromatic nucleus. Under similar conditions, 1-phenylethanol [44] was oxidized with a 99.5% yield to acetophenone, but dodecanol [50] gave a poor selectivity to dodecanal because of the hydration of the aliphatic aldehyde.

Oxidation of 9-decen-1-ol to 9-decen-1-oic acid, where both reactant and product were insoluble in water, was conducted on Pt–Bi/C catalysts suspended either in a dioxane–water mixture or in water [67] (see Section 3.3). The reaction was slower in the second case due to a less favorable contact between the four phases (water, organic substrate, solid, gas), but the selectivity was almost similar (83% at total conversion).

2.6. *Catalyst preparation*

Most of the studies on liquid phase oxidation reactions were conducted on platinum or palladium catalysts supported on active carbon or on alumina. Carbon supports (activated carbon and graphite) present the advantage of a high stability under all reaction conditions, particularly at low pH and in the presence of complexing molecules. However, activated carbon was found to be responsible for the deactivation in oxidation of 1-methoxy-2-propanol [42]. Different types of commercial catalysts, particularly the 5%Pt–5%Bi/C (CF 196RA/W), and 5%Pd–5%Bi (CE 196 RA/W) catalysts from Degussa have been used in various investigations. Catalysts were also prepared by impregnation (solvent evaporation or dry impregnation), by anionic adsorption ($PtCl_6^{2-}$ solution at acidic pH), and by cationic exchange ($Pt(NH_3)_4^{2+}$ solution at basic pH). This latter technique was the most reproducible one to obtain carbon-supported, platinum or palladium particles smaller than 2 nm, uniformly distributed in the catalyst pores, and with the highest stability to sintering, because of their anchoring to functional groups present on the carbons. Reduction of catalyst precursors were performed in the gas phase (H_2) or in the liquid phase (formaldehyde + KOH). Metal promoters such as bismuth or lead, were added to platinum-metals by co-impregnation, impregnation of the supported noble metal catalyst with an aqueous promotor salt solution, or redox surface reaction. A very simple and efficient way to load bismuth on Pt/C or Pd/C catalysts is to add required amount of $BiONO_3$ water solution into a suspension of the catalyst in a solution of formaldehyde or reducing sugar such as glucose [14,60]. Bimetallic (Pt–Bi) or trimetallic (Pt–Pd–Bi) catalysts are available commercially from Degussa [84].

Bönnemann et al. [85,86] have prepared Pt, Pd and Pt, Pd colloidal metal particles by reduction of the metal chloride in THF. The colloidal particles stabilized by tetraoctylammonium chloride were adsorbed on active charcoal coated with 5 wt.% bismuth. The resulting 5%$[Pd_{88}Pt_{22}]$–5%Bi/C catalyst, containing an homogeneous distribution of 3.6 nm particles, was found more active and stable for the oxidation of glucose to gluconate than the industrial Pt–Pd–Bi/C catalyst prepared by co-impregnation. The surfactant used for the stabilization of the colloids also acts as a modifier of the catalyst surface.

Wenkin et al. [87] prepared various Pd–Bi alloys to investigate their role in the catalytic oxidation of glucose by thermal decomposition of carboxylates.

Gold catalysts supported on active carbon and alumina were prepared by incipient wetness impregnation or by precipitation at basic pH using aqueous solutions of $HAuCl_4$ [88].

3. Case studies

3.1. Oxidation of carbohydrates

3.1.1. Glucose to gluconic acid

Besson et al. [59] have studied the oxidation of concentrated glucose solution (1.7 mol l^{-1}) on carbon-supported Pd–Bi/C catalysts of homogeneous size and composition (5 wt.% Pd, Bi/Pd = 0.1) prepared by deposition of bismuth on the surface of 1–2 nm palladium particles via a redox surface reaction [60]. The rate of glucose oxidation to gluconate was 20 times higher on Pd–Bi/C catalysts ($Bi/Pd_s = 0.1$) than on Pd/C. Table 1 gives the product distribution in four successive catalyst recycles. The selectivity was 99% or higher on the fresh and recycled catalysts. Furthermore, there was no bismuth leaching. These results were interpreted in terms of bismuth protecting palladium from over-oxidation because of its stronger affinity for oxygen (Fig. 1).

3.1.2. Oxidation of gluconic acid to 2-ketogluconic acid

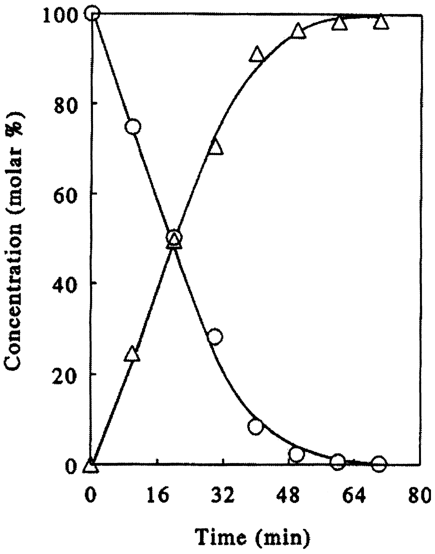

Fig. 3. Oxidation of sodium gluconate without pH control of the reaction. Evolution of the concentration (mol%) of the substrate and the reaction products during the oxidation. Sodium gluconate = 50 mM, catalyst (5%Bi/5%Pt/C) = 6.25 g/l, $T = 338$ K, $p(O_2) = 0.2$ atm, starting $pH_0 = 6$, final $pH_f = 4.4$ [34], (○) sodium gluconate; (△) 2-keto-gluconate.

Platinum catalysts can oxidize D-gluconate **1** into D-glucarate **2** or 2-keto-D-gluconate **3**, the latter being a valuable intermediate prepared by a fermentation process [89]. Smits et al. [10,11] showed that the selectivity to 2-keto-D-gluconate **3**, can be improved by lead promoter deposited on Pt/C catalysts. However, in this investigation, as well as in that of Besson et al. [63] where the reaction was also conducted at basic pH, the yield in 2-ketogluconate was limited by the formation of degradation products. Abbadi and van Bekkum [34] reinvestigated this reaction on 5%Bi/5%Pt/C catalyst, starting from sodium gluconate, but without regulating the pH. Fig. 3 indicates that the oxidation reaction proceeded almost to completion giving a 98% selectivity to the

Table 1
Product distribution in glucose oxidation[a]

Catalyst[b] (run)	Conversion[c] (%)	Yield[d] (mol%)				Selectivity (%)
		1	**2**	**3**	**4**	
Pd–Bi/C (1st)	99.6	99.4	<0.4	<0.4	0.2	99.8
Pd–Bi/C (2nd)	99.7	98.9	<0.4	0.6	0.2	99.1
Pd–Bi/C (3rd)	99.8	98.5	0.4	0.8	0.2	98.7
Pd–Bi/C (4th)	99.9	98.5	0.4	0.7	0.2	98.6
Pd–Bi/C (5th)	99.9	99.1	<0.4	0.6	0.2	99.2
Pd/C	82.6	78.1	1.4	2.3	0.7	94.6

[a] Reaction conditions: 1.7 mol l^{-1}, $T = 313$ K, pH 9; [glucose]/[Pd] = 787; air at atmospheric pressure.

[b] 4.7 wt.% Pd; Bi/Pd = 0.1.

[c] After 155 min on Pd–Bi/C and 24 h for Pd/C.

[d] **1**: Gluconate; **2**: 2-ketogluconate; **3**: 5-ketogluconate + glucarate, **4**: fructose.

desired product. The better selectivity at $pH < 6$ was attributed to a selective complexation of the promoter with the carboxyl and α-hydroxyl group of the gluconic acid whereas in alkaline medium the promoter is probably able to coordinate bidentatively with other hydroxyl groups. The resulting products are not stable and are oxidatively degraded. In the same way, arabinonate and ribonate were converted almost quantitatively to the corresponding 2-ketoaldonates [34].

A patent describing the oxidation of D-glucose and D-gluconic acid to 2-keto-gluconic acid has been issued by Abbadi et al. on Pt–Bi catalysts [90] and by Cerestar [91] on Pt–Pb catalysts in essentially the same reaction conditions as that described in [34].

3.1.3. Oxidation of lactose to lactobionate and 2-keto-lactobionate

Lactose, an abundant carbohydrate extracted from milk, can be valorized by oxidation to lactobionate and 2-keto-lactobionate (1-carboxylactulose) (Fig. 4).

Lactobionic acid is an acidulent and complexing agent in the food and pharmaceutical industry, and it is used for the preparation of biodegradable surfactants. The catalytic oxidation of lactose with air was described comparatively early [14,92]. Hendriks et al. [14] reported a 100% selectivity to sodium lactobionate up to 95% conversion on Pd–Bi/C catalysts at 333 K and in the pH range 7–10. The maximum initial reaction rate, $0.47\,\text{mol}\,\text{kg}^{-1}\,\text{s}^{-1}$ was obtained at a molar ratio $\text{Bi/Pd} = 0.50–0.67$; this rate was limited by O_2 mass transfer. The catalyst was recycled 15 times without significant loss of activity and selectivity.

Abbadi et al. [37] have studied the oxidation of lactose and sodium lactobionate to 2-keto-lactobionate which can be used to prepare new surfactants. The oxidation of lactose on Pt–Bi/C catalyst at pH 7 conducted transiently to lactobionate which was subsequently converted to 2-keto-lactobionate with a final yield of ca. 80%, because the conversion of lactobionate was incomplete. Starting from lactobionate without pH control, 2-keto-lactobionate was obtained with a 95% selectivity, but the oxidation reaction stopped at 50% conversion due to the poisoning of the Pt–Bi/C catalysts. Operating at pH 8, or replacing the catalyst by a fresh one, improved temporarily the conversion, but the inhibition of the catalyst persisted.

3.1.4. Oxidation of L-sorbose to 2-keto-L-gluconic acid

The oxidation of L-sorbose to 2-keto-L-gulonic acid (2-KLG) on platinum catalysts was extensively studied by the Swiss group at ETH Zürich [46,49,52–54]. The targeted product is an intermediate in the synthesis of vitamin C. The catalytic oxidation reaction was aimed at replacing the oxidation with mineral agents involved in the Reichstein–Gruessner synthesis [93]. Using unpromoted $5\%\text{Pt/Al}_2\text{O}_3$ catalyst in a reactor working in a transport limited regime, the best catalytic performance was a 39% yield (67% selectivity at 58% conversion) at neutral pH. Upon promoting with bismuth or lead the initial reaction rate improved, but the 2-KLG yield was even lower (25% yield at Bi/Pt wt/wt $\text{ratio} = 0.09$) [46]. Rapid dissolution of promotors was observed. Attempts to run the reaction at higher pH resulted in a further drop of selectivity because of the instability of 2-KLG at high pH, even in the absence of a catalyst. Therefore the idea was to modify the surface of metal catalysts with

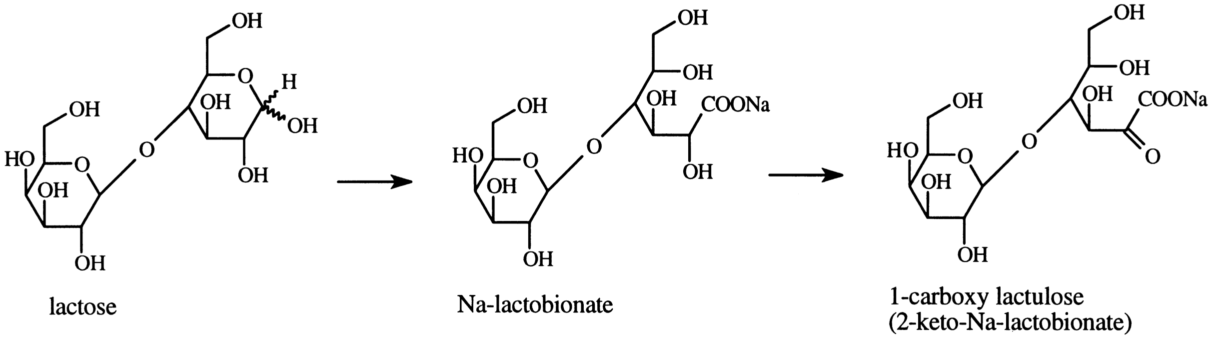

Fig. 4. Oxidation of lactose to Na-lactobionate and 1-carboxy lactulose (2-keto-Na-lactobionate).

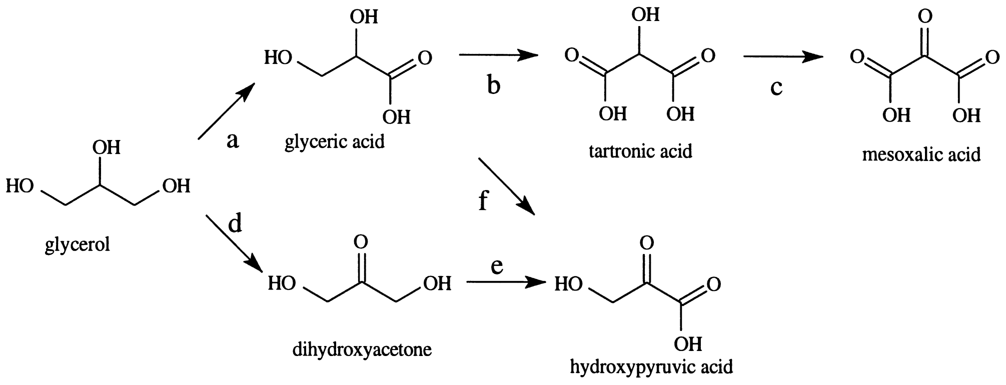

Fig. 5. Reaction pathways to oxygenated derivatives of glycerol.

adsorbed nitrogen bases without influencing significantly the pH of the reaction solution [49]. Rate and selectivity enhancements were obtained with the basic modifier adsorbed on the metal as suggested by electrochemical experiments. The best results were obtained with the addition of hexamethylenetetramine (HMTA) on Pt/C catalyst (HMTA/Pt$_s$ mol/mol = 0.1), leading to a selectivity increase from 51 to 95% at 30% conversion [52]. Rate acceleration was proposed to be due to the amine catalyzed hydration of the intermediate aldehyde to a geminal diol. The selectivity enhancement was explained by the formation of a complex between one of the hydroxyl groups of the carbohydrate and a nitrogen atom in HMTA. The adsorption of this complex on platinum surface results in a tilted position whereby only C-1 is exposed to oxidative dehydrogenation. Selectivities to 2-KLG were also improved (66% at 50% conversion) upon addition of trace amounts of phosphines in the reaction medium, particularly tributylphosphine, but the improvement was lower than with amines [53,54].

3.2. *Oxidation of glycerol and derivatives*

Glycerol is a highly functionalized molecule available from biosustainable resource, e.g. by transesterification of triglyceride obtained from rapeseed and sunflower crops. Thus, it is a clear candidate for use as a feedstock in the manufacture of the oxygenated derivatives represented in Fig. 5. These products presently have a very limited market because they are produced by costly stoichiometric or enzymatic processes. However, they are potentially valuable chelating agents (particularly tartronic and mesoxalic acids) and useful intermediates in organic synthesis. Although all the oxidation reactions given in Fig. 5 have been explored recently [61–66,68–73], we will concentrate our attention on those giving the highest yields.

3.2.1. *Oxidation of glycerol to glyceric acid*

Garcia et al. [61] conducted the oxidation of glycerol (GLY) to glyceric acid (GLYAC) on palladium and platinum catalysts at basic pH. Fig. 6 gives the product distribution obtained at pH 11 at which the higher reaction rates were measured. The selectivity to glycerate was 70% at 100% conversion, with tartronate and oxalate as the main over-oxidation by-products. A small amount of dihydroxyacetone (DHA) was formed

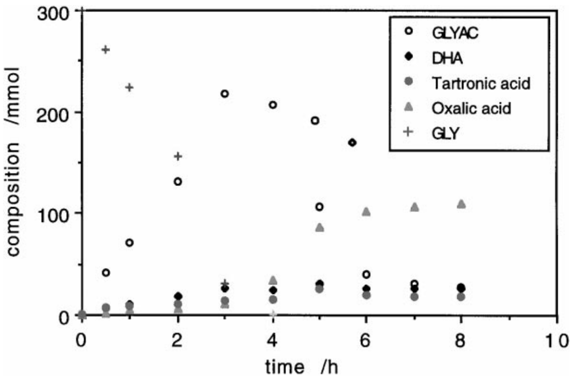

Fig. 6. Product distribution vs. time for glycerol oxidation at pH 11 on 5% Pd/C. Reaction conditions: 300 ml glycerol (10 wt.%), 1.5 g catalyst, 333 K, air flow rate 0.75 ml min^{-1} [61].

Table 2
Oxidation of secondary alcohols to ketones [43]

Catalysts	α-Tetrol[a]		Diphenyl carbinol[b]		1-Phenyl ethanol[c]	
	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)	Conversion (%)	Selectivity (%)
Bi–Pt/Al_2O_3	99	95	99	100	97	99.5
Pt/Al_2O_3	34	–	1.5	–	7.5	99

[a] Catalyst/ROH = 0.1; Li_2O_3/ROH = 0.01; surfactant/ROH = 0.05; $T = 358$ K; reaction time = 5 h.
[b] Catalyst/ROH = 0.01; Li_2O_3/ROH = 0.01; surfactant/ROH = 0.003; $T = 348$ K; reaction time = 3 h.
[c] Catalyst/ROH = 0.02; Li_2O_3/ROH = 0.01; surfactant/ROH = 0.01; $T = 333$ K; reaction time = 4.5 h.

but the selectivity to this product was dramatically improved (37% DHA at 70% glycerol conversion) on bismuth-promoted platinum catalyst.

3.2.2. *Oxidation of glyceric acid to* β*-hydroxypyruvic acid*

β-hydroxypyruvic acid is an important chemical intermediate for the preparation of different chemicals, particularly L-serine. Fordham et al. [62] studied calcium glycerate oxidation on 5%Pt–1.9%Bi/C catalyst without pH regulation; the maximum yield was of 64% at 80% conversion at acidic pH (3–4). In contrast, on the same catalyst under basic condition (pH 10–11) a 83% yield in tartronate was obtained with at 85% conversion of glycerate. This confirms the importance of acidic pH to obtain a selective complexation of the promoter with the carboxyl and α-hydroxyl group of the glyceric acid leading to a selective oxidation of the secondary alcohol function. In a similar investigation, Abbadi and van Bekkum [36] conducted the oxidation of sodium glycerate on 5%Bi–5%Pt/C catalyst without pH regulation. The pH decreased from 5.7 to 4.1 and 93% selectivity to β-hydroxypyruvic acid at 95% conversion was achieved.

3.2.3. *Oxidation of tartronic acid to mesoxalic acid*

Mesoxalic acid is a good chelating agent and potentially a valuable synthon for organic synthesis. Fordham et al. [66] have studied the preparation of mesoxalic acid by oxidation of sodium tartronate on Pt–Bi/C catalyst at 60°C without pH control; the maximum yield was 65% at 80% conversion. A total conversion of tartronic acid was obtained at 80°C giving 50% yield of mesoxalic acid without other by-products because they were totally oxidized into CO_2.

3.3. *Oxidation of alcohols*

3.3.1. *Oxidation of cinnamyl alcohol and insoluble secondary alcohols*

The oxidation of cinnamyl alcohol (Ph–CH=CH–CH_2OH) to cinnamaldehyde studied by Mallat et al. [45,50] was conducted in the presence of a surfactant (dodecylbenzene-sulfonate of sodium) because the molecule is not soluble in water. The oxidation was carried out at basic pH obtained by addition of Li_2CO_3 in the presence of Bi–Pt/Al_2O_3 catalyst and by controlling the air flow rate to avoid over-oxidation of the metal. The maximum selectivity to cinnamaldehyde 98.5% at 95.5% conversion was obtained with a ratio $Bi/Pt_s = 0.5$. Operating under similar conditions, i.e. in the presence of surfactants and Pt–Bi catalysts ($Bi/Pt_s = 0.5$), Mallat et al. [43] obtained good yields in ketones by oxidation of secondary alcohols (97–99% conversion and 95–100% selectivity) as shown in Table 2.

3.3.2. *Oxidation of 9-decen-1-ol in 9-decenoic acid*

Crozon et al. [67] have studied the oxidation of 9-decen-1-ol (rosalva) to 9-decenoic acid on palladium or platinum catalysts. Rosalva, as well as the corresponding aldehyde and acid were insoluble in water. Dioxane and water mixtures were used since they are miscible in all proportions. Homogeneous mixtures containing at least 50% dioxane to dissolve 1.2 wt.% of 9-decen-1-ol were employed for the oxidation reaction.

Fig. 7 indicates that under basic pH the oxidation of rosalva on Pt–Bi/C gave a quantitative yield in the desired product. The initial rate ($60\,\mathrm{mol\,h^{-1}\,mol_{Pt}^{-1}}$) was limited by gas–liquid mass transfer of oxygen. In the absence of bismuth, the selectivity to the unsaturated acid was 83% and the reaction rate was slower.

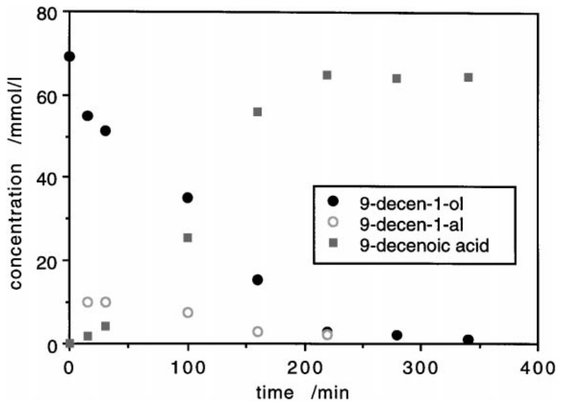

Fig. 7. Oxidation of 9-decen-1-ol on 4.58%Pt–2.95%Bi/C (molar ratio Bi/Pt = 0.45) at pH adjusted to 8. Temperature 323 K, 23 mmol 9-decen-1-ol, 1 g catalyst, 300 ml 50/50 dioxane/water [67].

The oxidation of decanol under the same conditions was rapid which indicated that the presence of the C=C bond in the alkyl chain had an adverse effect. This was probably due to a strong adsorption of the C=C bond which prevent the adsorption and dehydrogenation of the unsaturated alcohol.

3.3.3. *Oxidation of 1,2-propanediol on gold catalysts*

Catalytic oxidation of vicinal diols to α-hydroxy carboxylates were carried out by Prati and Rossi [88] in alkaline aqueous solution using gold based catalysts prepared by deposition–precipitation with sodium carbonate from $HAuCl_4$ solutions on active carbon suspension. The 1% Au/C catalysts had remarkable properties with respect to conventional Pt/C and Pd/C catalysts in terms of selectivity and stability. Thus, Table 3 shows that, at controlled pH of 8, 1,2 propanediol was very selectively oxidized to lactic acid, which indicates that gold exhibited a higher selectivity for the oxidation of the primary alcohol function than platinum and palladium. The activity of gold catalysts was also very stable as conversion proceeded or after several recycles indicating that gold is less sensitive to over-oxidation and/or self-poisoning than platinum and palladium.

3.3.4. *Recent patented alcohol oxidation processes*

A number of patents describing selective oxidation reactions of alcohols to the corresponding acids have been issued in the past 10 years. A few examples are given hereafter. Merat et al. [94] claimed that hydroxymethylfurfural (HMF) can be oxidized on Pt–Pb/C catalysts prepared by different methods (5 wt.% Pt with respect with HMF) into 2,5-furan dicarboxylic acid with yields in excess of 95%. The product is used for preparation of polymers with improved mechanical properties.

Aqueous solutions of 1,3 propanediol were oxidized at pH 11 in the presence of palladium catalysts (2.8% Pd with respect to 1,3-propanediol); the maximum yield in malonic acid was 86.1% [95]. Malonic acid can also be produced by oxidation of aqueous solutions (10 wt.%) of 3-hydroxypropionaldehyde (HPA) in the presence of 3%Pd/C catalysts and at pH 8. Complete conversion was achieved with high amounts of catalyst (33 wt.% Pd with respect to HPA) with a 96.7% yield [96]. Starting from 3-hydroxypropionic acid the yield in malonic acid was 95.4% at 97% conversion.

Aqueous solution (10 wt.%) of 3-hydroxypropionaldehyde were oxidized in the presence of 5%Pt/C catalysts (28 wt.% Pt with respect to HPA) into 3-hydroxypropionic acid, an intermediate used to prepare pharmaceutical and agricultural products. The best yield, obtained without pH regulation, was 92.9% at 97.2% conversion [97].

A few Japanese patents describe the synthesis of chemical intermediates from glycerol. Oxida-

Table 3
Oxidation of 1,2-propanediol to lactic acid on gold catalyst[a] [80]

Catalyst	*t* (h)	*T* (K)	LA (mol%)	HYDR (mol%)	PYR (mol%)	Conversion (%)	Selectivity (%)
1% Au/C	10	363	30	–	–	30	100
5% Pd/C	5	343	5	13	8	46	11
5% Pt/C	5	343	18	24	4	56	32

[a] Reaction conditions: diol/metal = 1000, T=343 K, p(O_2) = 100 kPa, pH regulated at 8 with NaOH 0.1 M. PYR = pyruvate; HYDR = hydroxyacetone; LA = lactate.

tion of glycerol over Pd/C at pH 8–13 yields 54% sodium glycerate [98]. Amination of glyceric acid, by treating with aqueous NH_3 and Pt/C, yields 38% serine [99]. This aminoacid could also be obtained by oxidation over Pt/C of serinol [100], prepared by reductive amination of dihydroxyacetone [101], which can also be catalytically prepared by selective oxidation of glycerol over Pt–Bi/C [61,70]. Oxidation of glycerol at constant pH 10 in the presence of 0.6%Ce–1.2%Bi–3%Pd/C yielded 90.6% sodium tartronate, useful as a detergent builder or for polymers [102]. Similarly, ketomalonic (mesoxalic) acid, was prepared by complete oxidation of tartronic acid in the presence of Bi–Pt/C with a selectivity of 95% [103].

A patent from Monsanto [104] disclosed the oxidation of alkaline solutions of various amino alcohols and polyethylene glycol in the presence of bimetallic catalysts prepared by deposition of copper on the surface of platinum. High yields to the corresponding carboxylates were reported.

Solution of methacrolein in methanol and aqueous soda solutions were continuously oxidized by O_2 at 5 bar and 80°C in a reactor packed with Pd–Bi/ SiO_2–MgO–Al_2O_3 catalyst. Methyl methacrylate was obtained with a 90.8% selectivity at 63.4% conversion [105].

4. Concluding remarks

Liquid phase oxidation with air on supported metal catalysts gives high selectivities which in certain cases, such as glucose oxidation, can match or surpass those of enzymatic processes. In addition, metal-catalyzed oxidations give comparatively high productivities, e.g. up to $8\,\text{mol}\,\text{h}^{-1}\,\text{g}_{\text{Pd}}^{-1}$ for glucose oxidation on Pd–Bi catalysts [39]. These processes offer the important advantages of high simplicity of operation (“one pot” reaction) and they are environmentally friendly since almost no harmful effluents are generated.

For industrial applications, metal catalyst should be repeatedly recycled or used in continuous mode for a long time. This implies the absence of irreversible deactivation due to significant leaching of the metal, promoters and the supporting material. Carbon supports are particularly recommended because of their stability in acidic medium. Platinum and palladium metals are resistant to leaching and to deactivation by over-oxidation. Gold catalysts are even more promising in that respect, but further evaluation of their selectivities and activities are required. On the other hand, p-electron promoters such as bismuth are easily leached away in acidic and oxidizing conditions and should be used in reactions carried out at controlled pH.

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