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Selective oxidation with air on metal catalysts

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Abstract

Oxidation of organic molecules with air on metal catalysts has been known for a long time but there has been a renewed interest in recent years because these catalytic reactions are environmentally safe and could replace stoichiometric oxidations. This paper describes several oxidation reactions conducted either at high temperatures in the gas phase or at moderate temperatures in the liquid phase; in both cases they proceed via a mechanism of oxidative dehydrogenation on the metal surface. Ethylene glycol was converted to glyoxal at 550°C on Ag/SiC catalyst with a 70% yield provided promoters were added to the reaction feed (diethylphosphite or iodine) or deposited on the catalyst ($LiPO_4$ or H_3PO_4). The promoters improve the conversion and selectivity by modifying the structure and the oxygen concentration on the surface of silver. Oxidation of glyoxal to glyoxylic acid, glucose to gluconic acid and glycerol to various oxygenated derivatives were conducted in water at 60°C in the presence of carbon-supported palladium or platinum catalysts. Bismuth promoter, deposited on the platinum metals by redox reaction, improves the catalyst activity by preventing over-oxidation of the metal surface and favors the oxidation of secondary alcohol functions into keto-derivatives. At higher reaction temperatures, platinum catalysts produce C–C bond rupture with the formation of carboxylic acids with smaller chains. Thus, cyclohexanol was converted into C_6, C_5, and C_4 diacids with a 45% selectivity to adipic acid on Pt/C catalysts at 150°C.

Keywords: Platinum catalyst; Glucose oxidation; Glyoxal oxidation; Glycerol oxidation

1. Introduction

Catalytic oxidations of organic molecules proceed via different mechanisms, viz.: (i) enzymatic oxidation; (ii) free radical auto-oxidations initiated by transition metal cations; (iii) metal ion oxidation of coordinated substrates such as Pd^{II}-catalyzed oxidations of olefins (Wacker process); (iv) oxygen transfer to the organic substrate mediated by metaloxo or peroxo complexes; (v) oxidative dehydrogenation on metal surfaces. In this paper only the latter type of oxidation mechanism will be considered.

Catalytic oxidations of alcohols on metal surfaces were described by Davy even before the word "catalysis" was coined. In spite of their early discovery, these reactions were comparatively much less studied than oxygen transfer reactions catalyzed by transition metal oxides. Catalysts are supported or unsupported zerovalent metals of groups 8–11, usually platinum, palladium or silver, and the oxidizing agent is molecular oxygen. They are conducted either in the gas phase at high temperatures with short contact time, or in the liquid phase usually at temperatures lower than 80°C. Very schematically, the mechanism involves the dehydrogenation of the organic substrate on the metal surface whilst oxygen is needed to scavenge the adsorbed hydrogen from the surface. Since the organic substrate and oxygen are both adsorbed on the metal

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surface, it can be easily predicted that a delicate balance of both reactants will be required to avoid either over-oxidation of the surface, i.e., the formation of a strongly adsorbed oxygen layer preventing the dehydrogenative adsorption of the substrate, or over-oxidation of the molecule leading to degradation products and ultimately to total oxidation into carbon dioxide. The association of p-electron metals with platinum metals can prevent the over-oxidation of the metal surface, and thus the activity decay, or change the adsorption mode of the substrate, thus controlling the selectivity.

Liquid phase oxidations on metals were already employed during the last century for the oxidation of carbohydrates, however the subject took a definitive start with the work of Heyns et al. [1,2] who were able to propose a reactivity scale for the oxidation of the different functional groups on Pt/C catalysts. This field of research has matured over the last 15 years following a series of studies by Dutch groups at Eindhoven [3–18] and Delft [19–25]. A breakthrough was made with the discovery that the addition of metal promoters such as lead or bismuth to platinum or palladium results in profound modification of the activity and selectivity of catalysts [9,10,13,23–32]. A comprehensive survey on the oxidation of alcohols was published by Mallat and Baiker [33].

In the past few years we have studied various oxidation reactions in the gas or liquid phases to synthesize valuable intermediate products or fine chemicals [34–44]. Our main objective was to replace oxidation reactions conducted with mineral oxidizing agents, by clean catalytic processes using air as oxidizing agent and producing a minimum of waste. The environmental and economical benefits of using heterogeneous oxidation catalysts for the production of fine chemicals were recently advocated by Sheldon and Dakka [45].

2. Experimental

The gas phase oxidation of ethylene glycol to glyoxal (CHOCHO) was performed in a flow reactor, as described before [34]. Aqueous solutions of ethylene glycol (50 wt%) were vaporized in flowing nitrogen at 450°C and the flow was mixed at the entrance of the reactor with oxygen diluted with nitrogen so that under standard reaction conditions the molar ratio was $EG/O_2/H_2O/N_2=1:1.45:3.40:35$. The total flow rate in the reactor maintained at 550°C was $212\ l\ h^{-1}$ and the residence time on a fixed bed of Ag/SiC catalyst was 0.03 s. The mixture was quenched, immediately after passing through the catalyst bed, with a water-cooled condenser followed by a liquid nitrogen trap. Condensed products were analyzed by HPLC and GC at regular time intervals. The 5 wt% Ag/SiC catalyst was prepared from a silicon carbide support, with a specific surface area less than $0.1\ m^2\ g^{-1}$, by impregnation with an aqueous solution of silver nitrate in required amounts. After elimination of the solvent in a rotary evaporator at 80°C and overnight drying at 373 K, the impregnated support was treated at 773 K under flowing H_2 for 24 h. It was shown by SEM and STM [35] that the surface of the SiC grains was covered by a homogeneously spread, thin silver layer supporting silver particles.

In the series of experiments described in [34], diethylphosphite (DEP) was added in very low amounts (20 ppm) to the ethylene glycol solution to boost the selectivity. In the present series of experiments, instead of injecting continuously the phosphorous compound, the 5% Ag/SiO_2 catalyst was impregnated with solutions of Li_3PO_4 or H_3PO_4 to obtain 400 ppm phosphorus with respect to silver. In addition, experiments were carried out with continuous injection of iodine (20 ppm) into the ethylene glycol solution.

Liquid phase oxidations were carried out in well-stirred, thermostated batch reactors containing the aqueous solution of the substrate to be oxidized and a suspension of the catalyst in powder form. The concentration of solutions covered a wide range, e.g. for glucose oxidation to gluconate up to $1.7\ mol\ l^{-1}$ [39]. 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. Reactions were carried out with pH ranging from 2 to 13, but in many instances from 7 to 9. A constant pH was regulated by the addition of dilute alkali solutions via a pump under the control of a pH regulator. It was verified that the kinetics were not under mass transfer control by monitoring the oxygen pressure in the liquid phase with an oxygen sensor. Liquid phase reactions at temperatures higher than 100°C were conducted in an autoclave under air pressure. The reaction kinetics were followed by chromatographic analysis (HPLC and GC) of the reaction medium taken at periodic time intervals.

Platinum catalysts were prepared by ion-exchange of carbon supports such as active charcoal (CECA 50S, 1400 $m^2 g^{-1}$) and graphite (Lonza HSAG, 300 $m^2 g^{-1}$). Supports were first washed with hot hydrochloric acid to eliminate mineral impurities, then oxidized with sodium hypochlorite solutions (4.0% active chlorine) at 300 K for 24 h to create exchangeable carboxylic acid groups. Ion exchange was performed by stirring the support for 18 h under nitrogen atmosphere in ammoniacal solutions containing the required amounts of $Pt(NH_3)_4Cl_2$ salt. The suspension was filtered, washed with water, and dried overnight at 373 K under nitrogen atmosphere. Reduction was carried out in a glass cell under a flow of hydrogen by heating at 1 K min^{-1} from 298 to 573 K and maintaining this temperature for 2 h. The reduced catalyst was cooled to 300 K under hydrogen and finally brought into contact with air diluted with argon. Palladium catalysts were prepared in the same way using $Pd(NH_3)_4Cl_2$ salt. Platinum- or palladium–bismuth catalysts were prepared by introducing the required amounts of $BiONO_3$ in a suspension of Pt/C or Pd/C catalysts in glucose solution. Under these conditions bismuth adatoms were deposited on the surface of the metallic particles by a redox surface reaction

$$(Pd-H)_{surface} + BiO^+ \rightarrow (Pd-Bi)_{surface} + H_3O^+$$

The amounts of metals on the catalysts were determined by ICP-AES after acidic dissolution. Solutions were also analyzed after reaction to verify that metals were not leached away. The metal dispersion was determined by high resolution electron microscopy with a Jeol 100CX microscope on thin sections of the catalyst cut with a diamond knife ultramicrotome. The composition of the bimetallic particles was measured by STEM-EDX analysis at 1.5 nm spatial resolution.

3. Results and discussion

3.1. *Gas phase oxidative dehydrogenation of glyoxal*

Gas phase dehydrogenations and oxidative dehydrogenations on metal catalysts are rarely employed for syntheses of fine chemicals because it is feared that reactants and products may not sustain high temperatures without degradation. However, dehydrogenation or oxydehydrogenation of molecules can be carried out in continuous flow reactors with controlled short residence times on fixed-bed catalysts. Thus, in the BASF process of citral synthesis one important step is the preparation of isoprenal by oxidative dehydrogenation of isoprenol at 500°C on silver catalysts. In the same way, we have recently succeeded in preparing 2-coumaranone with a 80% selectivity at 90% conversion by dehydrogenation of the α-carboxymethylidene cyclohexanone at 250°C on Pd/Al_2O_3 catalysts [48].

The conversion of ethylene glycol to glyoxal is another example of gas phase oxidative dehydrogenation on metal catalysts. Glyoxal is a useful synthon in organic chemistry and a cross-linking agent acting as a hardener in various materials which is industrially prepared either by nitric acid oxidation of acetaldehyde or by oxidative dehydrogenation of ethylene glycol at high temperatures on unsupported silver particles. In a previous study [34], it was shown that this reaction can be carried out with a 5 wt% Ag/SiC catalyst rather than on unsupported silver catalyst, thus minimizing the amounts of silver involved in the process. Glyoxal yields higher than 70% were obtained at high conversion (99%) provided small amounts (20 ppm) of diethylphosphite (DEP) were vaporized with the 50% aqueous solution of ethylene glycol. The effect of DEP on the selectivity to glyoxal is clearly shown in Table 1. The improvement from 55% to 73% was obtained because the molar fraction of C_1 products (CO, CO_2, formaldehyde) decreased from 42% to 22% [34]. The present study was aimed at studying the influence on selectivity of the mode of phosphorus loading on silver, and the effect of iodine employed as promoter in the place of phosphorus.

The 5 wt% Ag/SiC catalyst was impregnated either with Li_3PO_4 or H_3PO_4 to obtain different amounts of

Table 1
Reaction data for the oxidation of ethylene glycol into glyoxal

Catalyst	Promoter (ppm)	Conversion (%)	Glyoxal yield (%)	Selectivity (%)
Ag/SiC	0	96	53	55
Ag/SiC	20 ppm DEP	99	72	73
Ag/SiC+Li_3PO_4[a]	0	97	68	70
Ag/SiC+H_3PO_4[a]	0	97	69	71
Ag/SiC	80 ppm I_2	95	69	73

Reaction conditions: 550°C, residence time=0.06 s, $O_2/CH_2OHCH_2OH=1.45$.
[a] 414 ppm of P with respect to Ag.

phosphorus with respect to silver. An optimum effect on selectivity was obtained with 400 ppm of phosphorus with respect to silver. Table 1 indicates that the selectivity of the catalysts impregnated with Li_3PO_4 or H_3PO_4 was comparable to that obtained when continuous amounts of DEP were injected into the feed. This means that the selectivity enhancement was indeed due to phosphorus acting on the surface of the catalyst rather than as an inhibitor of radical type, gas phase oxidations leading to C_1 products.

However, the selectivity to glyoxal of the impregnated catalysts decreased gradually with time on stream so that after about 100 h, the selectivity was the same as that obtained with unpromoted catalysts whereas the continuous DEP injection allowed the 73% selectivity to be maintained. Analysis of the catalyst composition after reaction indicated that no phosphorus was present whatever the mode of promoter loading. Moreover, the amount of silver decreased from 5.6 to 4.8 wt% after 96 h on stream in the presence of DEP and from 5.6 to 3.7 wt% after 144 h on stream over the catalyst impregnated with Li_3PO_4. In the absence of phosphorous promoter, there was no leaching of silver. The STM and SEM studies of the catalyst surface indicated that the presence of phosphorous promoter prevented the sintering of silver into big plates and resulted in a fractal surface [35]. Therefore, the leaching of silver, which probably occurs as a result of the formation of a volatile compound with phosphorus, was accompanied by a permanent surface reconstruction. However, the effect of phosphorous promoters was probably not limited to maintaining a high surface specific surface since selectivity rather than activity was improved. The phosphorous promoters can rather act by modifying the oxygen concentration on the surface and thus the reaction pathway. Indeed, according to Capote and Madix [49,50], ethylene glycol can be oxidized on silver (1 1 0) crystal face via the following mechanism. The first step is the adsorption of ethylene glycol into 1,2-ethanedioxy species, OCH_2CH_2O, which can dehydrogenate into glyoxal:

$$(OCH_2CH_2O)_{ads} \rightarrow (OCH_2CH{=}O)_{ads} + H_{ads}$$

$$(OCH_2CH{=}O)_{ads} \rightarrow O{=}CHCH{=}O + H_{ads}$$

or react with adsorbed oxygen:

$$(OCH_2CH_2O)_{ads} + O_{ads} \rightarrow (O{=}CHCH_2O)_{ads} + OH_{ads}$$

$$(OCH_2CH_2O)_{ads} + OH_{ads} \rightarrow (O{=}CHCH_2O)_{ads} + H_2O_{ads}$$

$$(O{=}CHCH_2O)_{ads} + O_{ads} \rightarrow HCOO_{ads} + H_2C{=}O$$

The C_1 products can be further converted into CO_2 or CO. The relative amounts of $(OCH_2CH_2O)_{ads}$ and O_{ads} present on the surface might determine the extent of the two pathways, one leading to glyoxal, the other to C_1 products. The presence of phosphorus on the surface could play a decisive role in this balance by decreasing the concentration of adsorbed oxygen to a level where reactions leading to C_1 products become less probable. However, excess phosphorus could deplete the concentration of surface oxygen which prevents the formation of 1,2-ethanedioxy species and decrease the conversion.

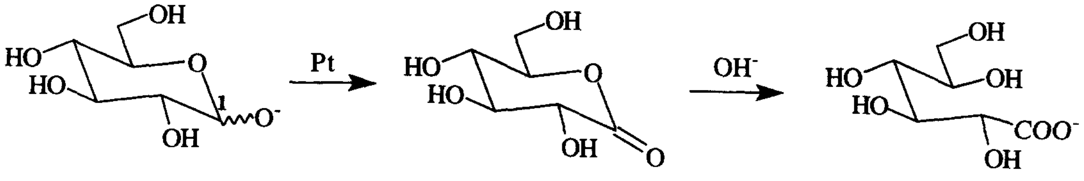
Table 1 shows that iodine injected continuously with ethylene glycol solution at a concentration of 80 ppm produced essentially the same effect as phosphorous as selectivity promoter. Iodine also produced a leaching of silver and prevented the sintering of silver particles on the SiC surface. Therefore, it is probable that iodine promoter acts in the same way as phosphorus on the composition and structure of the silver surface rather than as inhibitor of radical-type reactions in the gas phase.

3.2. Liquid phase oxidative dehydrogenation

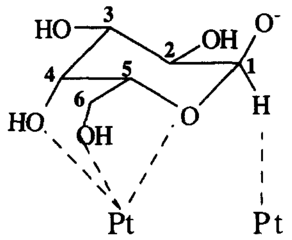
3.2.1. Generalities on mechanism

It was suggested, at a very early stage, that oxidations on metal surfaces proceed via a dehydrogenation mechanism. This is supported by the fact that isotopically labelled oxygen used as the oxidizing agent is not incorporated into reaction products [51] and by measurements showing that the electrochemical potential of the platinum catalysts in alcohol solutions is almost similar to that of the hydrogen electrode, which means that the Pt-surface is covered by adsorbed hydrogen [52]. Similar measurements during oxidation reactions also showed that the surface is partially covered with hydrogen [53]. A more complete account of the electrochemical literature data can be found in Ref. [33].

The dehydrogenation mechanism was also supported by the work of de Wit et al. [19] showing that aldoses dehydrogenate on platinum or rhodium catalysts at room temperature and basic pH (>11), yielding aldonates and molecular hydrogen which evolves from the reaction medium. In alkaline solutions containing fructose and glucose, and under nitrogen atmosphere, platinum or rhodium catalyze the dehydrogenation of glucose into gluconate, and, with the dissociated hydrogen thus available, the hydrogenation of fructose into mannitol and sorbitol [54]. The mechanism of dehydrogenation of unprotected aldoses in alkaline solutions was explained [19] by the formation of complexes between Pt-surface atoms and ionized aldose molecules followed by the abstraction and transfer on the metal surface of a hydride and thus the formation of a carbonyl group.



The different aldoses did not exhibit the same reactivity because of their different configuration; the adsorption of D-galactose depicted in the following scheme is very favorable because of the axial C_4 hydroxyl group, thus accounting for the highest reactivity of this carbohydrate.



If there is a general agreement on the dehydrogenation mechanism, the precise reaction pathway is still under debate [33,55]. Indeed, there are still too many uncertainties as to the nature and coverage of the adsorbed species on the metal surface (e.g., H or $H^{(-)}$, O or $OH^{(-)}$, RCH_2OH or RCH_2O^- or $RCH_2O\cdot$) which depend upon many factors such as pH, oxygen availability, carbohydrate concentration and nature of the metal.

3.2.2. Generalities on catalyst deactivation

In metal-catalyzed oxidations there is a risk of irreversible deactivation due to modifications of the metal phase in the course of reactions such as metal sintering (growth of particle size leading to a decrease of the active surface area) or metal leaching away in solutions. Characterization of platinum and palladium catalysts prepared by ion-exchange indicated little change in metal dispersion after glyoxal or glucose oxidation [36,39]. Schuurman et al. [17] reported a moderate sintering after five recyclings of platinum catalysts in methyl-α-glucoside oxidation which was explained by a mechanism of dissolution of the smallest particles and redeposition on the larger. Metal leaching, particularly of electropositive metal promoters should be of serious concern, especially when large amounts of these promoters are used; unfortunately, this point is not well documented in the literature. Interestingly, it was reported [23] that both platinum and aluminum from Pt/Al_2O_3 catalysts leach away in solutions of D-ribose and D-xylose but the platinum leaching is much larger for the former indicating that the configuration of this carbohydrate is more favorable for metal complexing.

In oxidation on metals, the specific cause of deactivation is the so-called oxygen poisoning of the metal surface. It is widely accepted that the metal surface of the working catalyst is partially covered by chemisorbed oxygen forming strong Pt–O (or Pt–OH) bonds. The current oxygen coverage of the surface will depend upon the relative affinity of the metal for oxygen and for the organic substrate. Dehydrogenation of the latter upon adsorption yields dissociated hydrogen which is scavenged by the chemisorbed oxygen to yield water. This can also be accounted for by redox equilibria involving surface metal atoms, with oxygen acting as oxidant and the carbohydrate as reductor. This dynamical balance of competitive adsorption controls the reaction rate both initially, and as reaction proceeds. The equilibrium tends to shift towards an overwhelming oxygen coverage as the concentration of the substrate in solution decreases, which poisons the reaction. However, Mallat et al. [33,46,56,57] pointed out that the presence of strongly adsorbed reaction products or by-products block part of the surface thus producing a genuine deactivation which ultimately favors surface over-oxidation resulting in a much greater deactivation. Various factors affect the initial rate and subsequent deactivation, some of them are given below.

(1) *Factors depending on the catalyst.* (a) Metals with a higher redox potential (or higher work function) will be less prone to oxidation [36,58]. In that respect, among Pt-group metals, platinum catalysts will be the less easily poisoned by over-oxidation, followed by palladium. (b) Small metal particles (e.g., <2 nm) deactivate more readily than larger ones, as shown in the oxidation of methyl-α-D-glucoside on platinum catalyst [15] and in a study of D-glucose oxidation on Pd/C catalysts (see Section 3.2.3) where the particle size dependent deactivation was attributed to the stronger affinity of oxygen for small particles [38]. (c) Mass transfer limitation in catalyst pores may help prevent deactivation as demonstrated by van Dam et al. with their model of diffusion-stabilized catalysts [21]. In the course of oxidation reaction on porous extrudates where metal particles are uniformly distributed in pores, the concentration of oxygen decreases continuously from the edge to the core of the extrudates; therefore, there is always a zone at a certain depth, where the concentration of oxygen is optimum to avoid metal surface over-oxidation.

(2) *Factors depending on the species in solution.* (a) The higher the affinity of the carbohydrate for the metal, the lower the oxygen coverage. Thus, the absence of poisoning in the oxidation of 5-hydroxymethylfurfural on various platinum-group metals (including ruthenium, which is more prone to surface over-oxidation because of its comparatively low redox potential), was attributed to the strong bonding of the substrate via the π-electrons of the furan ring [22]. (b) The higher the reduction potential of the substrate, the lower will be the deactivation. Thus, no deactivation occurs for the oxidation of strong reductors like glyoxal [36]. 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. (c) Initial activity as well as deactivation depend markedly upon the pH: lower rates and high deactivation are observed for reactions run at acidic pH because undissociated carboxylic acids are very strongly adsorbed on metals [59]. They can poison the reaction, directly by blocking the surface, and indirectly by favoring over-oxidation processes. Not only reactants and main reaction products are involved but also any by-products such as diacids produced by further oxidation and rupture of the parent carbohydrate molecule. Obviously, any kind of molecules known to poison metal surfaces (e.g., sulfur compounds) will contribute to the deactivation.

(3) *Factors depending on the reaction conditions.* 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 the aqueous solutions will be totally consumed (the reaction rate is then limited by gas–liquid oxygen mass transfer) and the risk of over-oxidation is weak. For sluggish reaction, over-oxidation can be prevented by working at low and constant concentration of oxygen by dilution with nitrogen or by taking advantage of mass transfer limitation in pores (vide supra). Monitoring the electrochemical potential of the catalyst to control the optimum oxygen supply is a good way to cope with this problem [47,53].

Table 2
Oxidation of glyoxal into glyoxylic acid on platinum catalysts (40°C, air at atmospheric pressure)

Catalysts	Particle size[d] (nm)	Glyoxal (mol l^{-1})	Conversion (%)	Glyoxylic acid yield (%)	Selectivity (%)
5% Pt/C[a]	1–3	0.35	96	70	73
4% Pt/C[b]	1–2	0.35	88	47	53
1.8% Pt/C[b]	1–2	0.9	93	29	31
4.6% Pt/graph.[c]	1–2	0.9	94	54	57
6% Pt/SiO_2	1.5–2.5	0.35	19		
14% Pt/Y zeolite	1	0.1	90	35	39

[a] Commercial catalyst with an egg-shell metal distibution.
[b] Catalyst prepared by ion exchange with a uniform distribution of particles.
[c] HSAG12 (470 $m^2 g^{-1}$) Lonza graphite.
[d] Measured by TEM on ultramicrotome sections.

3.2.3. Glyoxal oxidation into glyoxylic acid

Gloxylic acid (CHOCOOH) is a highly reactive synthon entering into the preparation of various fine chemicals (e.g., vanillin and penicillin). It is industrially prepared by nitric acid oxidation of glyoxal and it is a tough challenge to replace this stoichiometric process by a selective catalytic process because of the propensity of the molecule to oxidize further into oxalic acid. We attempted to oxidize aqueous glyoxal solutions with air on metal catalysts because of the mild conditions required, the lack of noxious reactants and products and the feasibility for catalyst recycling [36,37,60]. Reactions were carried out at 40°C in the presence of air at atmospheric pressure, by stirring a suspension of the catalyst in aqueous glyoxal solutions. In a first series of experiments, catalysts with different platinum metals (Pt, Ir, Pd, Rh, Ru) prepared on the same active carbon and with the same particle size (1 to 2 nm) were compared. The initial rate of reaction increased in the series 0=Ru<Rh<Pd<Ir<Pt, similar to the series of the redox potentials of these elements. Then, platinum catalysts on different supports were compared. Table 2 gives the conversion and selectivity data at the maximum glyoxylic acid yield.

SiO_2- and TiO_2-supported catalysts were almost inactive for the oxidation of glyoxal aqueous solutions under the present reaction conditions. This could be due to oligomeric glyoxal hydrogen-bonded to the hydroxyl groups of the oxide supports thus forming a strongly bound, immobile layer covering the support surface which prevents adsorption–desorption processes on the metal particles located on the support. In contrast, the zeolite-supported catalyst was active although the selectivity was low (39%). This may be due to the fact that the reaction takes place on platinum particles located in the zeolite supercages where glyoxal oligomers cannot form because of the limited space available.

The best glyoxylic acid yield (70% at 96% conversion) was obtained with the 5% Pt/C catalyst where the metal was distributed near the external surface of the active charcoal grain, and for the oxidation of moderately concentrated glyoxal solution (0.35 mol l^{-1}). For a similar concentration, the maximum glyoxylic acid yield was only 47% with the 1.8% Pt/C catalyst prepared by ion exchange, where the metal particles are uniformly distributed in the micropores of the support. The lower selectivity can be attributed to diffusional limitation in the micropores which increases the residence time of the reactants and products in the catalyst micropores so that glyoxylic molecules once formed have a higher probability to readsorb on metal particles and be oxidized further.

These diffusional effects in micropores were even worse as the concentration of the glyoxal solutions increased. Thus, the glyoxylic acid yield was only 29% for the oxidation of a 0.9 mol l^{-1} glyoxal solution on the 1.8% Pt/C catalyst where Pt-particles are uniformly distributed in the micropores. In contrast, the 4.6% Pt/graphite catalyst, where the particles are located on graphite steps and thus accessible from the liquid phase with less diffusional limitation, gave a 54% yield for the oxidation of the same glyoxal solution.

3.2.4. *Oxidation of glucose to gluconic acid*

D-Gluconic acid, used as a biodegradable chelating agent and employed as an intermediate in the food and pharmaceutical industry, is produced by enzymatic oxidation of glucose [61]. An alternative route of oxidation of glucose using bismuth-promoted, palladium catalysts, has been patented [28]. Unpromoted palladium catalysts can oxidize glucose but the rate of the reaction decreases with conversion, and side oxidation reactions decrease the selectivity. Thus, Besson et al. [38] have studied the oxidation of concentrated glucose solution (1.7 mol l^{-1}) on carbon-supported palladium catalysts with different particle size. The catalyst with particles larger than 3 nm gave complete conversion within 6 h (Fig. 1a), whereas the conversion almost reached a plateau at two-thirds conversion on catalyst with particles smaller than 2 nm (Fig. 1b). This was attributed to a particle size dependent,

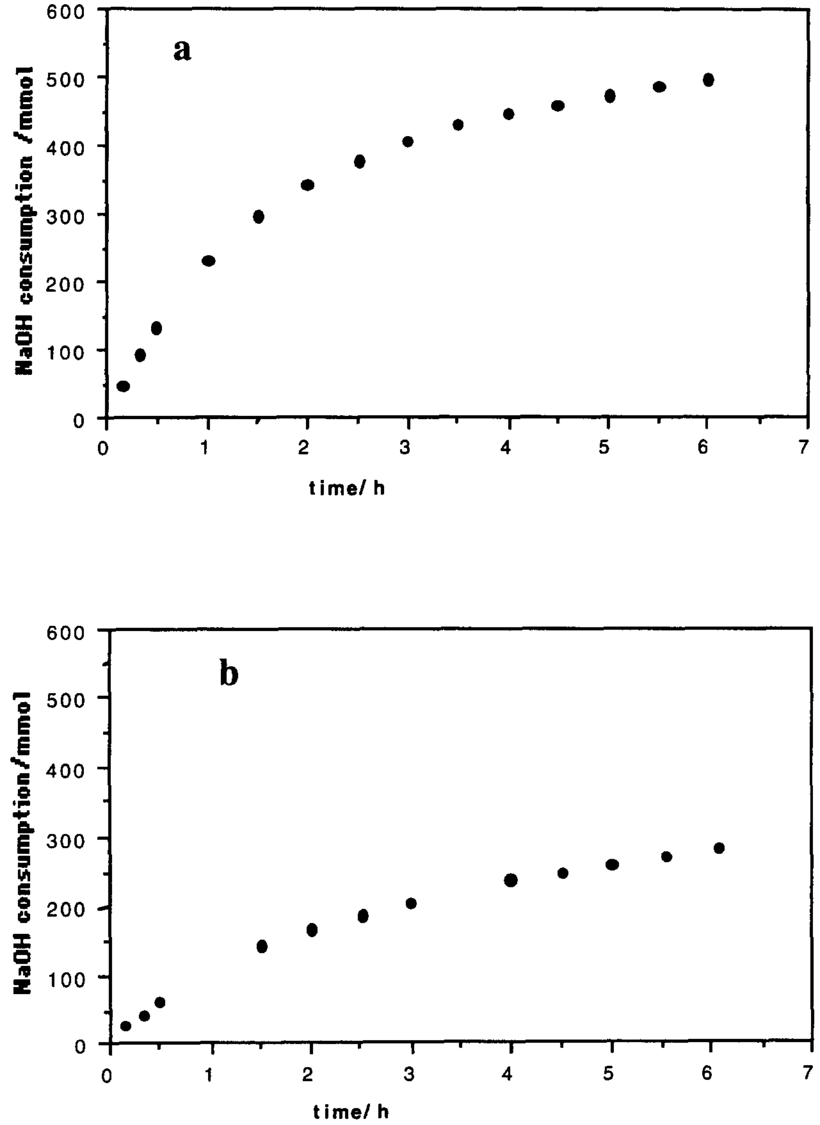


Fig. 1. Glucose oxidation on Pd/C catalysts with different particle size: (a) 3–10 nm particles; (b) 1–2.5 nm particles. (The conversion of glucose was monitored with the soda added to maintain a constant pH).

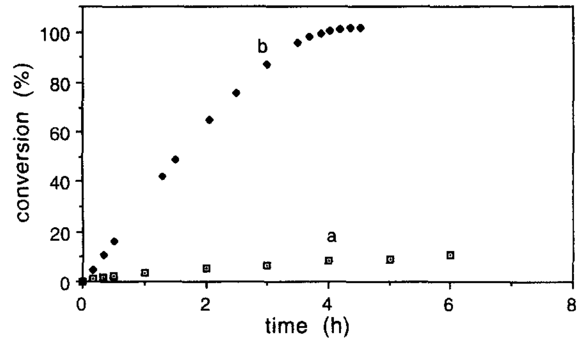


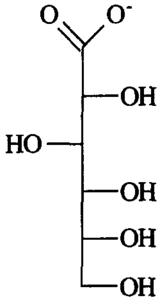
Fig. 2. Glucose conversion as a function of time on palladium catalysts: (a) Pd/C; (b) Pd–Bi/C with Bi/Pd=0.1. (T=313 K, pH=9, glucose/Pd=3150).

oxygen poisoning of the surface, the smaller particles being the most prone to over-oxidation because of their stronger affinity for oxygen.

The beneficial effect of bismuth on the activity and selectivity was clearly demonstrated with Pd–Bi/C catalysts of homogeneous size and composition (5 wt% Pt, Bi/Pt=0.1) prepared by deposition of bismuth on the surface of 1–2 nm palladium particles via a redox surface reaction [39]. Fig. 2 shows that the rate of glucose oxidation is 20 times larger on Pd–Bi/C (Bi/Pd=0.1) than on Pd/C. At the same time, the selectivity to D-gluconate was greatly improved (99.8% at 99.6% conversion) probably because the rates of side reactions were negligible with respect to oxidation into gluconate. In addition, the catalyst exhibited excellent stability since following successive recyclings there was no bismuth leaching and the activity and selectivity were almost constant, as shown by the data given in Table 3. These results were interpreted in terms of bismuth protecting palladium from over-oxidation because of its stronger affinty for oxygen, evidenced by calorimetric measurements. It was proposed that glucose oxidation proceeds according to the oxidative dehydrogenation mechanism given in Fig. 3.

3.2.5. Oxidation of gluconic acid

Platinum catalysts can oxidize D-gluconate **1** into D-glucarate **2** or 2-keto-D-gluconate, the latter being a valuable intermediate prepared by a fermentation process [62]. 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. The selectivity to **3** was interpreted by the formation of a surface complex **4** where gluconate chelates the promoter atom via the oxygen atoms of the carboxyl group and α-hydroxyl group.



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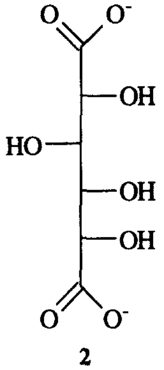

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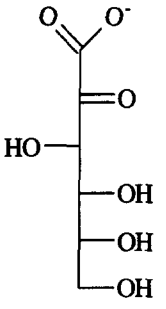

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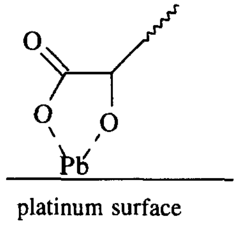

4

The effects of lead and bismuth on the selectivity of this reaction were reinvestigated by Abbadi and van Bekkum [24,25]. Starting from sodium gluconate and without pH regulation, the oxidation proceeded to completion with an almost quantitative yield in **3** on a Pt–Bi/C catalyst (5 wt% Pt, 5 wt% Bi). Arabinonate and ribonate were in the same way, converted almost quantitatively to the corresponding 2-ketoaldonates.

The oxidation of gluconate on Pt-catalysts gives low yields of glucarate because of the formation of more oxidized products such as tartarate and oxalate. Thus, a 55% yield at 97.2% conversion was recently reported by Besson et al. [44] for this molecule which might be used as a biodegradable complexing agent in detergents. This yield was only slightly higher than those reported previously [3,8,9,11–13] but it was obtained with more concentrated solutions (2 mol l^{-1})

Table 3
Product distribution in glucose oxidation after successive recyclings of Pd–Bi/C

Run	Conversion (%)	Yield[a] (mol %)				Selectivity (%)
		1	2	3	4	
1	99.6	99.4	<0.4	<0.4	0.2	99.8
2	99.7	98.9	<0.4	0.6	0.2	99.1
3	99.8	98.5	0.4	0.8	0.2	98.7
4	99.9	98.5	0.4	0.7	0.2	98.6
5	99.9	98.1	<0.4	0.6	0.2	99.2

Reaction conditions: time 155 min; T=313 K; pH=9; glucose/Pd=787; Bi/Pd=0.1.
[a] 1 – gluconate; 2 – 2-ketogluconate; 3 – 5-ketogluconate+glucarate; 4 – fructose.

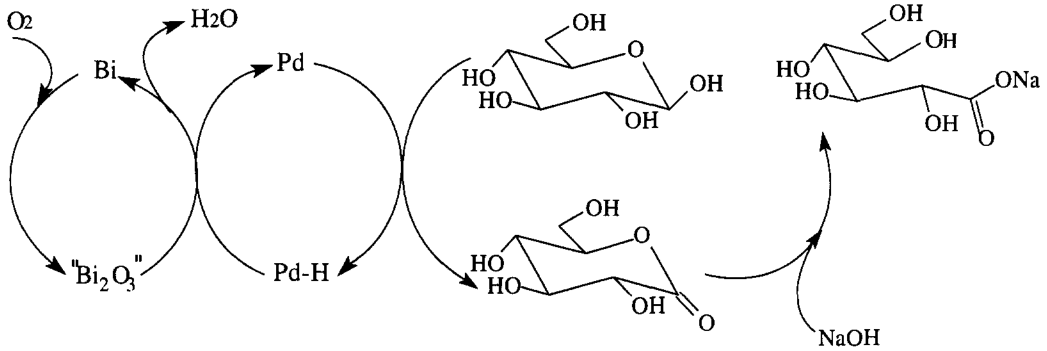

Fig. 3. Scheme for the mechanism of glucose oxidation on Pd–Bi catalysts.

and comparatively lower amounts of catalyst (gluconate/Pt=787). Platinum catalysts were more prone to deactivation by over-oxidation for gluconate oxidation because gluconate is a weaker reductor than glucose. It was shown that Pt–Au bimetallic catalysts were more resistant to deactivation. The addition of gold adatoms on the surface of platinum may decrease the adsorption energy of oxygen and possibly of acidic side products which contribute to surface poisoning.

3.2.6. *Glycerol oxidation*

Glycerol is a highly functionalized molecule available from biosustainable resource (triglyceride-containing crops such as rapeseed and sunflower). Thus, it is a clear candidate for use as a feedstock in the manufacture of the oxygenated derivatives represented in Fig. 4. 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. The main objective of this work was to control the chemoselectivity of metal catalysts for the oxidation of the primary and secondary alcoholic functions of glycerol (GLY) to give the full range of possible oxygenated derivatives: glyceric acid (GLYAC), dihydroxyacetone (DHA), hydroxypyruvic acid (HYPAC), tartronic acid (TARAC) and mesoxalic acid (MESAC). This was achieved by using tailored platinum or palladium catalysts where the metal surface is modified with bismuth adatoms [40,41,42]. Table 4 gives the maximum yields obtained for the different reactions.

In the absence of bismuth promoter or at basic pH, the primary alcohol functions are preferentially oxidized to carboxylic acids (reaction **a**, **c**, **e**). The corresponding aldehydes should be formed transiently but their rates of oxidation are much larger than those of alcohols so that they cannot be detected in the reaction medium. Thus, a 70% yield in glyceric acid was obtained from glycerol on palladium catalyst and

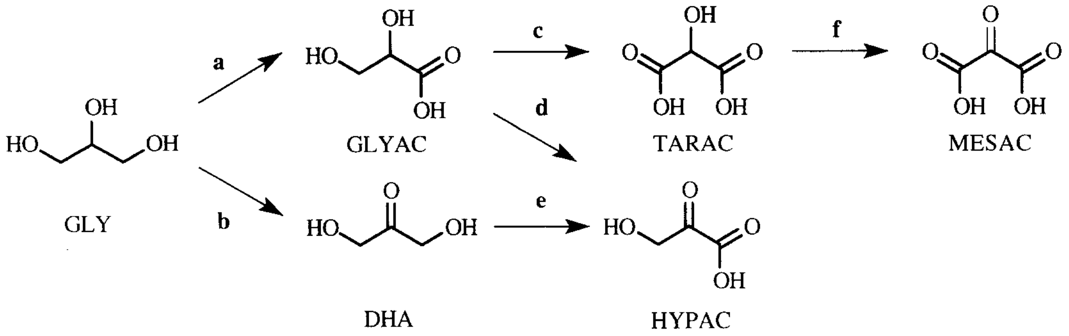

Fig. 4. Reaction pathways to oxygenated derivatives of glycerol.

Table 4
Activity and selectivity data for the oxidation of glycerol and oxygenated derivatives

Reaction[a]	Catalyst	Preparation method[b]	pH	Concentration (mol l^{-1})	Initial rate[c]	Max. yield[d] (%)
a	Pd	1	11	1	110	70
b	Pt–Bi	2	1.5–2	1	50	37
c	Pt–Bi	2	10–11	0.1	300	83
d	Pt–Bi	2	3–4	0.1	250	74
e	Pt	3	6	0.3	40	35
f	Pt–Bi	4	1.5	0.1	210	39

[a] See Fig. 4.

[b] 1, impregnation; 2, coimpregnation; 3, exchange; 4, surface redox deposition of bismuth.

[c] $\mathrm{mol\,h^{-1}\,mol^{-1}_{(Pd\,or\,Pt)}}$.

a 83% yield in tartronic acid was obtained from glyceric acid (Table 4).

Secondary alcohol functions (reactions **b**, **d**, **f**) were oxidized selectively on bismuth-promoted platinum catalysts at acidic pH. Thus, glycerol oxidation into DHA was performed with 80% initial selectivities but the catalyst deactivated with time which may be due to the accumulation of strongly adsorbed acids on the surface. The highest DHA yield was 37% at 75% conversion. Glyceric acid oxidation proceeded rapidly to give high yields of hydroxypyruvic acid (74% at 77% conversion). A proposed mechanism for this reaction is depicted in Fig. 5, where the formation of a complex between bismuth atoms and the glycerate leads to the selective oxidation of the secondary alcohol function. Tartronic acid was oxidized to mesoxalic acid on Pt–Bi/C at pH=1.5 with a 39% yield at 53% conversion. The conversion rate of tartronic acid was high at first but decreased as the reaction proceeded, probably because the formed mesoxalic acid was more strongly adsorbed on the surface than tartronic acid. Subsequently, the initial high selectivity tapered off due to over-oxidation.

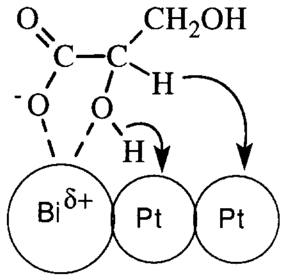

Fig. 5. Proposed mechanism for oxidation of the secondary alcohol function of glyceric acid.

3.2.7. *Cyclohexanol oxidation*

At low oxidation temperatures, such as those reported for alcohol oxidation (vide supra), there is little or no C–C bond breaking of organic molecules on metal catalysts. However, at higher temperatures

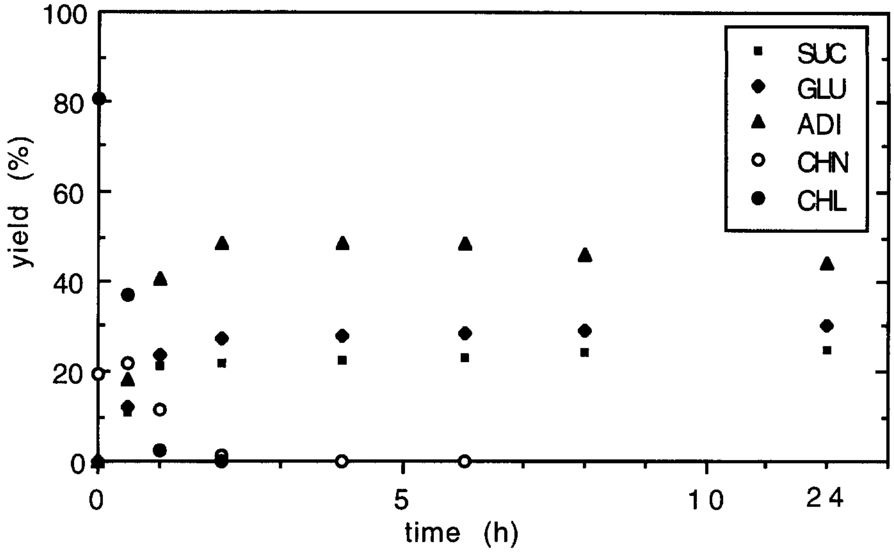

Fig. 6. Product distribution vs. time in the oxidation of aqueous solutions of cyclohexanol (50 mmol l^{-1}) on Pt/C catalyst at 150°C and 5 MPa air pressure (CHL=cyclohexanol, CHN=cyclohexanone, ADI=adipic acid, GLU=glutaric acid, SUC=succinic acid).

molecules can be increasingly oxidized and ultimately entirely converted into CO_2. This is the basis of catalytic wet air oxidation for the treatment of organic effluents in water. Thus, maleic acid was totally converted into CO_2 at 130°C on platinum catalysts [63]. The oxidation of organic substrates with limited C–C bond cleavage could be used to produce valuable chemicals. Thus, it was shown recently [43] that platinum supported on active charcoal was an effective catalyst for the oxidation with air of cyclohexanol to produce diacids such as adipic acid. Fig. 6 shows that at 423 K and 5 MPa air pressure cyclohexanol was converted into diacids with a selectivity of 45% for adipic acid, 30% for glutaric acid and 25% for succinic acid. The nature of the formed products suggests that the oxidative cleavage of the cyclohexanol proceeds through several parallel pathways to the dicarboxylic acids. The first reaction consists of a cleavage of the C_1–C_2 bond, followed by oxidation of the terminal functions. Lower carbon chain acids, like glutaric and succinic acids arise through oxidative cleavages of the C_2–C_3 and C_3–C_4 bonds. Formic and oxalic acids are probably formed transiently, but under these reaction conditions, they would be easily oxidized to CO_2 [63].

4. Concluding remarks

The few examples given above show that 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 mol h^{-1} g_{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 effluents are generated. These catalytic oxidations can be extended to produce valuable oxygenated intermediates from other sustainable resources.

Although mainly batch operations have been carried out so far, reactions could well be performed in continuous mode in fixed-bed catalytic reactors provided active carbon extrudates are used as supports in place of carbon powders. These reactors would provide the additional advantage of better control of the contact time of reactants and products with the catalyst which may lead to additional gains in selectivity.

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 and because the formation of immobile layers of hydroxylated substrates, which cause diffusional limitation on the catalyst surface, is less probable than on oxide supports. Platinum group metals are thermodynamically stable in the zerovalent state in a wide range of conditions so that leaching could be easily avoided. On the other hand, bismuth atoms not directly bonded to platinum atoms are easily leached away in acidic and oxidizing conditions. With low Bi/Pt ratios and reactions carried out at controlled pH, bismuth leaching can be avoided as shown in the case of glucose oxidation [39].

References

[1] K. Heyns and H. Paulsen, Angew. Chem., 69 (1957) 600, Adv. Carbohydr. Chem., 17 (1962) 169.

[2] K. Heyns, H. Paulsen, G. Ruediger and J. Weyer, Fortschr. Chem. Forsch., 11 (1969) 285.

[3] H.G.J. de Wilt and H.S. van der Baan, Ind. Eng. Chem. Prod. Res. Develop., 11 (1972) 374.

[4] H.G.J. de Wilt, J. Lindhout and B.F.M. Kuster, Carbohydr. Res., 19 (1971) 5.

[5] H.G.J. de Wilt, J. Lindhout and B.F.M. Kuster, Carbohydr. Res., 23 (1972) 333.

[6] H.G.J. de Wilt, J. Lindhout and B.F.M. Kuster, Carbohydr. Res., 23 (1972) 343.

[7] J.M.H. Dirkx, H.S. van der Baan and J.M.A. van den Broek, Carbohydr. Res., 59 (1977) 63.

[8] J.M.H. Dirkx and H.S. van der Baan, J. Catal., 67 (1981) 1.

[9] J.M.H. Dirkx and H.S. van der Baan, J. Catal., 67 (1981) 14.

[10] P.C.C. Smits, B.F.M. Kuster, K. van der Wiele and H.S. van der Baan, Carbohydr. Res., 153 (1986) 227.

[11] P.C.C. Smits, B.F.M. Kuster, K. van der Wiele and H.S. van der Baan, Appl. Catal., 33 (1987) 83.

[12] P.J.M. Dijkgraaf, M.J.M. Rijk, J. Meuldijk and K. van der Wiele, J. Catal., 112 (1988) 329.

[13] P.J.M. Dijkgraaf, H.A.M. Duisters, B.F.M. Kuster and K. van der Wiele, J. Catal., 112 (1988) 329.

[14] H.E.J. Hendriks, B.F.M. Kuster and G.B. Marin, Carbohydr. Res., 204 (1990) 121.

[15] Y. Schuurman, B.F.M. Kuster, K. van der Wiele, G.B. Marin, in: P. Ruiz, B. Delmon (Eds.), New Developments in Selective Oxidation by Heterogeneous Catalysis, Elsevier, Amsterdam, 1992, p. 43.

[16] Y. Schuurman, B.F.M. Kuster, K. van der Wiele and G.B. Marin, Appl. Catal. A, 89 (1992) 31.

[17] Y. Schuurman, B.F.M. Kuster, K. van der Wiele and G.B. Marin, Appl. Catal. A, 89 (1992) 47.

[18] J.H. Vleeming, F.A. de Bruijn, B.F.M. Kuster, G.B. Marin, in: B. Delmon, G. Froment (Eds.), Catalyst Deactivation, Elsevier, Amsterdam, 1994, p. 467.

[19] G. de Wit, J.J. de Vlieger, A.C. Kock-van Dalen, R. Heus, R. Laroy, A.J. van Hengstum, A.P.G. Kieboom and H. van Bekkum, Carbohydr. Res., 91 (1981) 125.

[20] H.E. van Dam, A.P.G. Kieboom and H. van Bekkum, Appl. Catal., 33 (1987) 361.

[21] H.E. van Dam, P. Duijverman, A.P.G. Kieboom and H. van Bekkum, Appl. Catal., 33 (1987) 373.

[22] P. Vinke, H.E. van Dam, H. van Bekkum, in: G. Centi, F. Trifiro (Eds.), New Developments in Selective Oxidation, Elsevier, Amsterdam, 1990, p. 147.

[23] F.R. Venema, J.A. Peters and H. van Bekkum, J. Mol. Cat., 77 (1992) 75.

[24] A. Abbadi and H. van Bekkum, Appl. Catal. A, 124 (1995) 409.

[25] A. Abbadi and H. van Bekkum, J. Mol. Cat. A, 97 (1995) 111.

[26] P.C.C. Smits, Akzo N.V. EP 151498 (1985).

[27] H. Saito, S. Ohnaka, S. Fukuda, Kawaken Kao Corp., EP 142725 (1985).

[28] P. Fuertes, G. Flèche, Roquette Frères, EP 233816 (1987).

[29] B.M. Despeyroux, K. Deller, E. Peldszus, in: G. Centi, F. Trifiro (Eds.), New Developments in Selective Oxidation, Elsevier, Amsterdam, 1990, p. 159.

[30] K.B. Kokoh, P. Parpot, E.M. Belgsir, J.M. Leger, B. Beden and C. Lamy, Electrochim. Acta, 38 (1993) 1359.

[31] C. Brönnimann, Z. Bodnar, P. Hug, T. Mallat and A. Baiker, J. Catal., 150 (1994) 199.

[32] P. Verdeguer, N. Merat and A. Gaset, J. Mol. Cat., 85 (1993) 327.

[33] T. Mallat and A. Baiker, Catal. Today, 19 (1994) 247.

[34] P. Gallezot, S. Tretjak, Y. Christidis, G. Mattioda and A. Schouteeten, J. Catal., 142 (1993) 729.

[35] P. Gallezot, S. Tretjak, Y. Christidis, G. Mattioda, A. Schouteeten, Y.W. Chung and T.S. Sriram, Catal. Lett., 13 (1992) 305.

[36] P. Gallezot, R. de Mésanstourne, Y. Christidis, G. Mattioda and A. Schouteeten, J. Catal., 133 (1992) 479.

[37] P. Gallezot, F. Fache, R. de Mésanstourne, Y. Christidis, G. Mattioda, A. Schouteeten, in: L. Guczi, F. Solymosi, P. Tétényi (Eds.), New Frontiers in Catalysis, Proceedings of the 10th International Congress on Catalysis, Elsevier, Amsterdam, 1993, p. 195.

[38] M. Besson, P. Gallezot, F. Lahmer, G. Flèche, P. Fuertes, in: J.R. Kosak, T.A. Johnson (Eds.), Catalysis of Organic Reactions, vol. 53, Marcel Dekker, New York, NY, 1993, pp. 169–180.

[39] M. Besson, P. Gallezot, F. Lahmer, G. Flèche and P. Fuertes, J. Catal., 152 (1995) 116.

[40] R. Garcia, M. Besson and P. Gallezot, Appl. Catal. A, 127 (1995) 165.

[41] P. Fordham, M. Besson and P. Gallezot, Appl. Catal. A, 133 (1995) L179.
[42] P. Fordham, R. Garcia, M. Besson, P. Gallezot, in: J.W. Hightower, W.N. Delgass (Eds.), Proceedings of the 11th International Congress on Catalysis, Paper A11.
[43] J.C. Beziat, M. Besson and P. Gallezot, Appl. Catal. A, 135 (1996) L7.
[44] M. Besson, G. Flèche, P. Fuertes, P. Gallezot and F. Lahmer, Recl. Trav. Chim. Pays-Bas, 115 (1996) 217.
[45] R.A. Sheldon and J. Dakka, Catal. Today, 19 (1994) 215.
[46] T. Mallat, Z. Bodnar, A. Baiker, in: S.T. Omaya, J.W. Hightower (Eds.), Catalytic Selective Oxidations, ACS Symp. Series, vol. 523, Washington, DC, 1993, p. 308.
[47] T. Mallat and A. Baiker, Catal. Today, 24 (1995) 143.
[48] J.C. Vallejos, A. Perrard, Y. Christidis, P. Gallezot, EU Patent No. 95401385.0-2110 (14/06/95, Société Française Hoechst).
[49] A.J. Capote and R.J. Madix, J. Am. Chem. Soc., 111 (1989) 3570.
[50] A.J. Capote and R.J. Madix, Surf. Sci., 214 (1989) 276.
[51] M. Rottenberg and Baertschi, Helv. Chim. Acta, 227 (1956) 1073.
[52] E. Müller and K. Schwabe, Z. Electrochim. Acta, 33 (1928) 170.
[53] T. Mallat, Z. Bodnar, A. Baiker, in: M. Guisnet, J. Barbier, J. Barrault, D. Duprez, G. Perot, C. Montassier (Eds.), Hetrogeneous Catalysis and Fine Chemicals III, Elsevier, Amsterdam, 1993, p. 377.
[54] A.J. van Hengstum, A.P.G. Kieboom and H. van Bekkum, Starch, 36 (1984) 317.
[55] P. Vinke, D. de Wit, A.T.J.W. de Goede, H. van Bekkum, in: P. Ruiz, B. Delmon (Eds.), New Developments in Selective Oxidation by Heterogeneous Catalysis, Elsevier, Amsterdam, 1992, p. 1.
[56] T. Mallat, Z. Bodnar, M. Maciejewski, A. Baiker, in: V. Cortès Corberan, S. Vic Bellon (Eds.), New Developments in Selective Oxidation II, Elsevier, Amsterdam, 1994, p. 561.
[57] T. Mallat, Z. Bodnar, A. Baiker, O. Greis, H. Strübig and A. Reller, J. Catal., 142 (1994) 237.
[58] H. E van Dam, L.J. Wisse and H. van Bekkum, Appl. Catal., 61 (1990) 187.
[59] W.M. Sachtler, J. Fahrenfort, in: Proceedings of the 2nd International Congress on Catalysis, Technip, Paris, 1961, p. 831.
[60] R. de Mésanstourne, P. Gallezot, EP 0 438 948 B1 (08/12/93).
[61] H. Hustede, H.J. Haberstroh, E. Schinzing, in: B. Elvers, S. Hawkins, M. Ravenseroft, J.F. Rounsaville, G. Schulz (Eds.), Ullmann's Encyclopedia of Industrial Chemistry, vol. A12, VCH, Weinheim, 1989, p. 449.
[62] H. Röper, in: F.W. Lichtenthaler (Ed.), Carbohydrates as Organic Raw Materials, VCH, Weinheim, 1991, p. 267.
[63] P. Gallezot, N. Laurain and P. Isnard, Appl. Catal. B, 9 (1996) L11.