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Catalytic oxidation with air of tartronic acid to mesoxalic acid on bismuth-promoted platinum

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Mesoxalic acid (ketomalonic acid) was prepared by oxidative dehydrogenation with air of tartronic acid in aqueous solution on carbon-supported platinum–bismuth catalysts. By increasing the pH, using a higher catalyst/substrate ratio or increasing the temperature, higher yields could be obtained (maximum yield obtained of 65% at 80% conversion). The results obtained for this reaction and for the analogous catalytic oxidations of glyceric acid to hydroxypyruvic acid, and lactic acid to pyruvic acid, enabled a general reaction mechanism to be proposed for the selective oxidation of α-hydroxy acids to α-keto acids on platinum–bismuth catalysts.

Keywords: mesoxalic acid (ketomalonic acid), tartronic acid, selective catalytic oxidation, platinum–bismuth metal catalysts

1. Introduction

The use of platinum metals as catalysts for the selective oxidation of alcohols with air to the corresponding aldehydes, ketones or carboxylic acids has become a highly active research domain due to its potential application to fine chemical production. For example, a wide range of useful substances may be obtained by selective catalytic oxidation of glycerol **a** with air on precious metals (see figure 1). Oxidation of the primary function is favoured on platinum or palladium catalysts, to give glyceric acid **b** [1,2] and, subsequently, tartronic acid **c** [3,4]. The rate of glycerol conversion increases with pH, with maximum yields being obtained at pH$\geqslant$9. However, on bismuth-promoted platinum, and in acidic media, the selectivity may be altered to favour oxidation of the secondary hydroxy function. Thus high yields of dihydroxyacetone **d** were obtained from glycerol [1,5] and hydroxypyruvic acid **e** was obtained from glyceric acid. The oxidation of tartronic acid to mesoxalic acid **f** was recently reported [6].

As a highly functionalised molecule, mesoxalic acid has potential use as a complexing agent and as a precursor in organic synthesis, but its present high cost limits application. The production of this substance using a bio-sustainable feedstock (glycerol) by means of a heterogeneous process employing a supported metal catalyst, water as solvent and air as oxidising agent would reduce the market value. The clean chemistry features of this reaction (non-polluting, non-toxic effluents, recyclable catalyst) are also highly appealing.

Aqueous solutions of tartronic acid were oxidised on platinum-catalysts under acidic conditions. A brief study on the influence of the pH, temperature and the catalyst / substrate ratio on reaction progress was carried out.

2. Experimental

2.1. Mesoxalic acid oxidations

Oxidations were carried out in a glass batch reactor, fitted with stirrer, gas supply lines, oxygen sensor

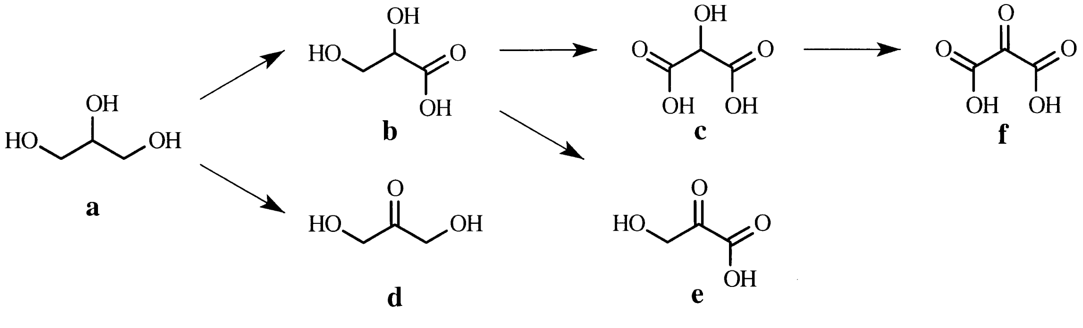

Figure 1. Products obtained from the catalytic oxidation of glycerol.

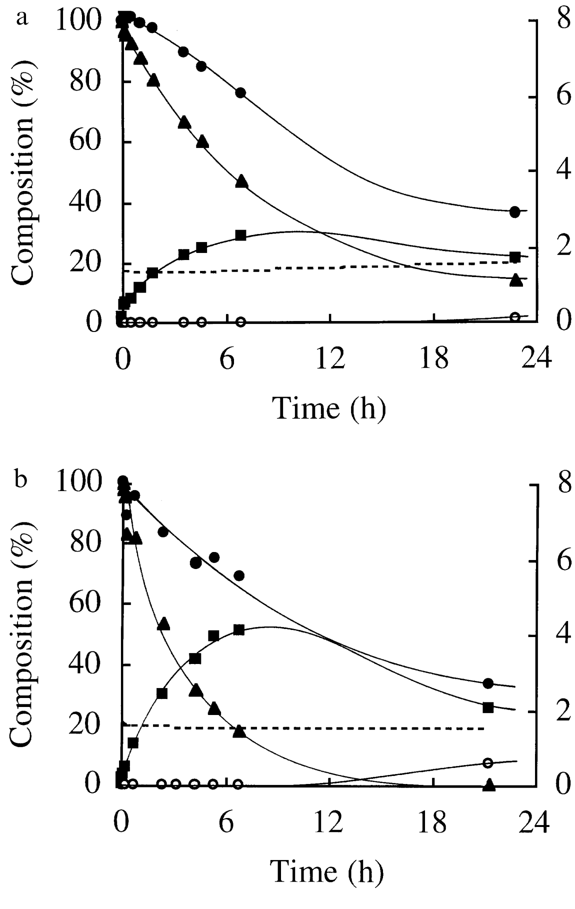

Figure 2. Product distribution obtained for the oxidation of tartronic acid (pH 1.5) at 50°C on (a) 5.7%Pt2.4%Bi/C catalyst (203 mg) and (b) 3.8%Pt4.8%Bi/C catalyst (1.02 g) as a function of time ((▲) tartronic acid, (■) mesoxalic acid, (○) oxalic acid, (●) total material balance, (- - -) pH).

(Ingold) and pH electrode (Radiometer). The catalyst was suspended in 300 ml of aqueous tartronic acid (0.1 mol ℓ^{-1}), agitated at 1200 rpm and heated to 323 K with a constant flow of nitrogen bubbling through the suspension. At the required temperature, the gas supply was switched to air (0.75 ℓ min^{-1}) and the pH could be maintained at a constant value by the addition of a solution of sodium hydroxide via a pump controlled by the pH meter. The temperature, oxygen pressure and pH were monitored throughout and samples of the reaction medium were periodically removed and analysed by HPLC. An ion exclusion column (Sarasep Car-H) with UV and RI detectors mounted in series, was employed to determine the degree of conversion and the concentration of oxidation products.

2.2. *Catalyst preparation*

Platinum-on-carbon catalysts were prepared by treating an active charcoal support (CECA 50S) with NaOCl (3%) to create oxidised sites on the surface, which were subsequently loaded by ion exchange with $Pt(NH_3)_4^{2+}$ ions. Reduction to the metal was accomplished by directing a steady hydrogen flow over the catalyst surface at 300°C. A surface redox reaction was subsequently used to deposit the bismuth promoter. The reduced platinum catalyst was suspended in a glucose solution, under an inert nitrogen atmosphere, and the required quantity of a solution of $BiONO_3$ in 1 M hydrochloric acid was added. The pH of the solution was adjusted to 9. The catalyst was filtered, washed and dried under vacuum at 100°C. TEM images indicated a metal dispersion consisting of particles smaller than 2 nm and analytical microscopy measurements indicated that the particles were of homogeneous composition [6]. Bismuth-promoted catalysts were also prepared by coimpregnation of the carbon support, with an acidic solution of $H_2PtCl_6/BiCl_3$ and reduction by the addition of formaldehyde and potassium hydroxide. A more heterogeneous particle size was thus obtained, however, analytical microscopy showed that these particles were bimetallic [1]. It was shown that both methods of preparation lead to nearly the same catalytic results [1,4].

3. Results

Figure 2a shows the conversion and evolution of products as a function of time, when the oxidation of tartronic acid was performed on 200 mg of 5.7%Pt2.4%Bi/C (Bi/Pt = 0.39; molar ratio tartronic acid/Pt = 514), without control of the pH (initial pH 1.5). The oxidation proceeded with an initial reaction rate of 220 mol h^{-1} mol$_{Pt}^{-1}$ and with an initial selectivity to mesoxalic acid of ca. 95%. But, as conversion progressed, over-oxidation of the product, reflected in the rapid decrease in the total material balance, led to reduced yields (maximum yield obtained: 29% at 53% conversion, after 7 h). After 22 h of reaction, the conversion was 86%; residual levels of oxalic acid were detected, but no other species were observed. When this experiment was performed under the same conditions but in the presence of a different catalyst, with a higher Bi/Pt ratio (4.1%Pt3.7%Bi/C; Bi/Pt = 0.85) similar results were obtained. When the molar ratio tartronic acid/Pt was reduced to 155, by increasing the quantity of catalyst (figure 2b), the oxidation of tartronic acid proceeded to total conversion and higher yields were obtained (50% of mesoxalic acid at 80% conversion). Mesoxalic acid was then slightly over-oxidised to oxalic acid and carbon dioxide.

Figures 3a and 3b show the results obtained for the oxidation of sodium tartronate performed at pH 5, with two different tartronic acid/Pt molar ratios (493 and 98, respectively). In figure 3a (tartronic acid/Pt = 493) the reaction proceeded with a much higher initial rate (540 mol h^{-1} mol$_{Pt}^{-1}$) and improved yields were obtained (39% at 79% conversion, after 6 h) when compared to acidic conditions. However, the rate of over-oxidation was also accelerated – the concentration of acid species

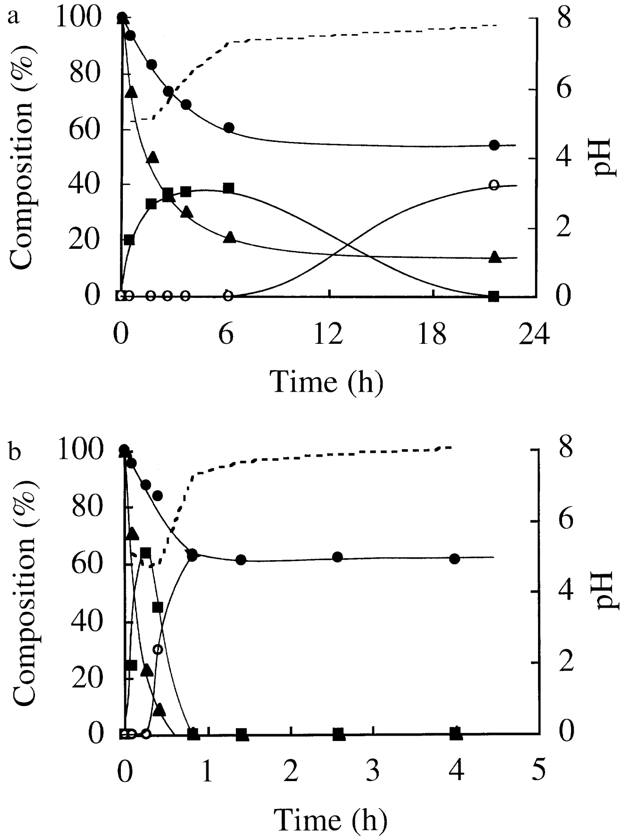

Figure 3. Product distribution obtained for the oxidation of sodium tartronate (pH 5) at 50°C on (a) 5.7%Pt2.4%Bi/C catalyst (212 mg) and (b) 5.25% Pt1.9%Bi/C catalyst (1.02 g) as a function of time ((▲) tartronic acid, (■) mesoxalic acid, (○) oxalic acid, (●) total material balance, (- - -) pH), with molar ratio tartronic acid/Pt = 493 and 98 for (a) and (b) respectively.

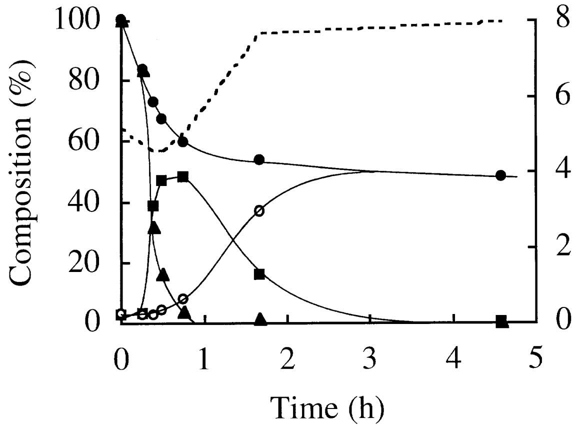

Figure 4. Product distribution obtained for oxidation of tartronic acid (pH 5) at 80°C on 5.7%Pt2.4%Bi/C catalyst (203 mg) as a function of time ((▲) tartronic acid, (■) mesoxalic acid, (○) oxalic acid, (●) total material balance, (- - -) pH).

fell, resulting in an increase in pH and dramatic developments in reaction progress. As the pH increased from 5 to 8, the conversion of tartronate was blocked and rapid complete over-oxidation occurred. Mesoxalic acid was oxidised to oxalic acid (relatively stable under these neutral conditions). With an increased amount of platinum (figure 3b), the reaction proceeded in a transport limited regime as shown by the measure of oxygen concentration in the reaction medium. The yields in mesoxalic acid were improved (65% at 80% conversion).

At pH 5, with an increase in the reaction temperature to 80°C (tartronic acid/Pt ratio = 515), the oxidation of sodium tartronate followed a similar path to that shown at 50°C, but on a much reduced time-scale (figure 4). At the beginning, this reaction was also diffusion controlled. A maximum yield of 50% at 96% conversion was observed after 1 h of reaction.

4. Discussion

Under acidic conditions, the secondary hydroxy function of tartronic acid may be selectively oxidised on platinum–bismuth catalysts to give mesoxalic acid. This type of reaction has been shown to occur for similar α-hydroxy carboxylic acids, such as glyceric acid [4,6], gluconic acid [8,9] and lactic acid [10], which were each oxidised to the corresponding keto acid on either platinum–bismuth or platinum–lead catalysts. It has been proposed that the selective oxidation of the secondary alcohol function of tartronic acid is driven by the formation of a complex, formed between neighbouring carboxylic and α-hydroxy groups of tartronic acid and bismuth atoms on the catalyst surface (figure 5), which leads to preferential oxidation of the α-hydroxy function [7].

The adsorption of free acids is assumed to be responsible for the catalyst deactivation observed under acidic

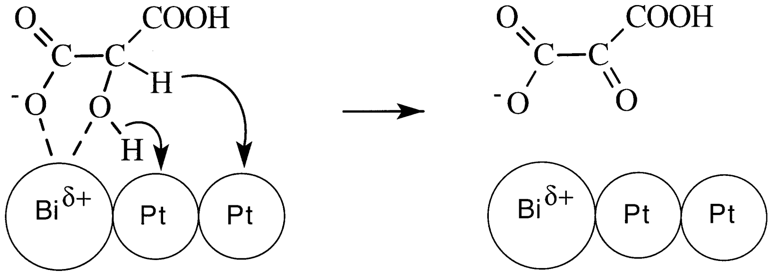

Figure 5. Proposed complexing mechanism for selective catalytic oxidation of the secondary hydroxy function of tartronic acid.

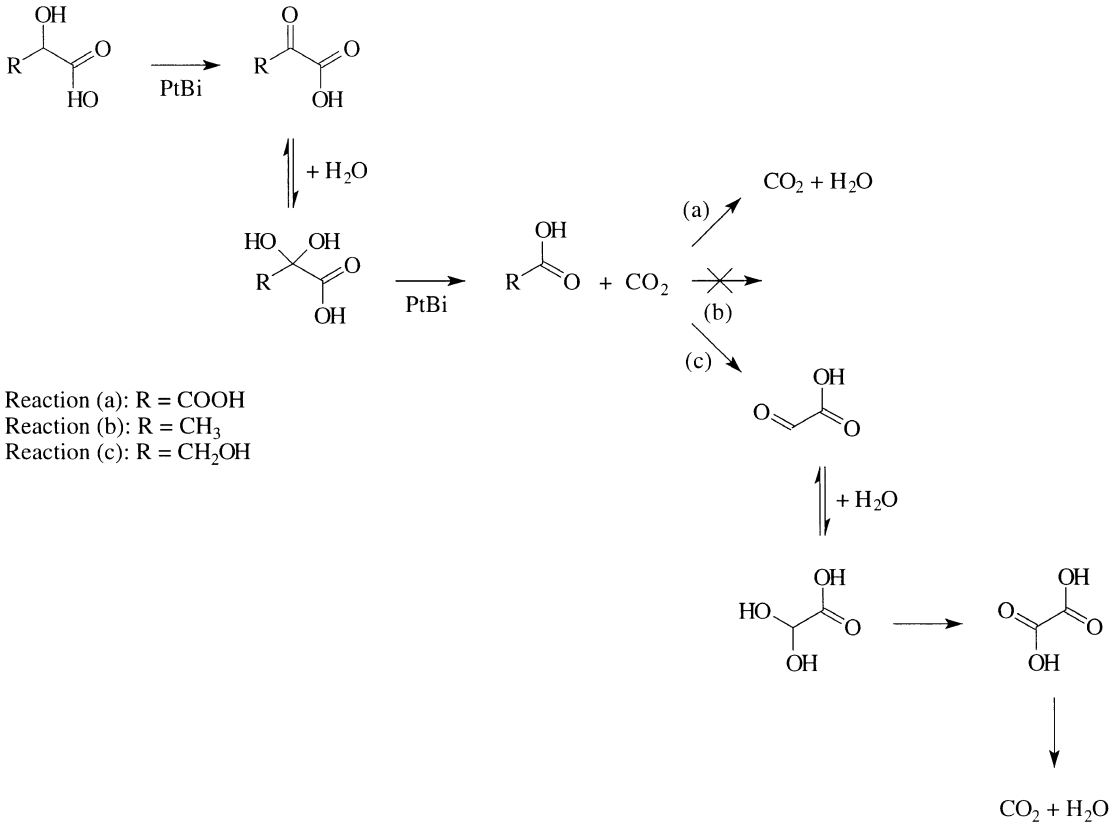

Figure 6. Proposed reaction scheme for the oxidation of tartronic acid on platinum–bismuth catalysts.

conditions (figures 2a and 2b). Neutralisation of the acids prevented deactivation and allowed higher yields to be obtained (figures 3a and 3b). A similar observation has been reported for the oxidation of gluconic acid on PtBi/C [9].

However, yield is essentially limited by an over-oxidation to oxalic acid and carbon dioxide. In fact, mesoxalic acid is particularly likely to form a geminal diol species [11], which would be easily oxidised on platinum catalysts to give oxalic acid and carbon dioxide. The rate of oxidation of the geminal diol species increases with pH as oxidation of primary alcohol does [12]. Thus, the rate of mesoxalic acid oxidation is relatively slow at pH 1.5 (figures 2a and 2b), but increases at pH 5, and accelerates rapidly at pH 8 (figures 3a, 3b and 4). With an increase in the catalyst to substrate ratio, or an increase in temperature, the rate of the main reaction is increased whilst the equilibrium between mesoxalic acid and its geminal diol is unchanged; thus higher yields are obtained.

This reaction has similarities with the aforementioned catalytic oxidations of glyceric acid to hydroxypyruvic acid and lactic acid to pyruvic acid, and a general mechanism for the oxidation of α-hydroxy acids to α-keto-acids on PtBi/C is proposed (see figure 6). Reaction (a): oxidation of tartronic acid to mesoxalic acid proceeds as described above, to give oxalic acid. Reaction (b): oxidation of lactic acid to pyruvic acid gives acetic acid. Reaction (c): oxidation of glyceric acid to hydroxypyruvic acid gives glycolic acid, via the geminal diol, and subsequently glyoxylic acid, via a second geminal diol, then oxalic acid (all these species have been observed and the results were reported previously [7]). The oxidation of lactic acid to pyruvic acid was performed by Tsujino et al. [10], but the presence of acetic acid as a product was not reported. This was almost certainly because acetic acid was itself used to prepare the ester derivatives of the acid produits prior to analysis by GC, and thus could not be observed. Having executed the same experiment in our laboratory, we can confirm that acetic acid is indeed evolved. The subsequent oxidation of this species is known to be difficult [13].

5. Conclusions

Mesoxalic acid is the end product of a series of catalytic oxidations with air, starting from glycerol via glyceric acid and tartronic acids. Good yields of mesoxalic acid were obtained by oxidation with air of tartronic acid on PtBi/C catalysts. Thus, a 65% yield at 80% conversion was obtained at 60°C, pH 5 and with a catalytic ratio tartronic acid/Pt of 155. However, to avoid the separation of mesoxalic and tartronic acids, it may be advantageous to obtain a total conversion of tartronic acid. Thus, by operating at pH 5 and 80°C, a 50% yield of mesoxalic acid was obtained with only traces of oxalic acid present.

The results obtained for this reaction, coupled with those obtained for the similar oxidations of glyceric acid to hydroxypyruvic acid and lactic acid to pyruvic acid on PtBi/C, enable a general mechanism for the catalytic oxidation of α-hydroxy acids to α-keto acids to be formulated.

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