Lead modified platinum on carbon catalysts for the selective oxidation of (2-) hydroxycarbonic acids, and especially polyhydroxycarbonic acids to their 2-keto derivatives

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LEAD MODIFIED PLATINUM ON CARBON CATALYSTS FOR THE SELECTIVE OXIDATION OF (2-) HYDROXYCARBONIC ACIDS, AND ESPECIALLY POLYHYDROXYCARBONIC ACIDS TO THEIR 2-KETO DERIVATIVES

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ABSTRACT

D-Gluconic acid has been oxidised with oxygen and air at 55 °C in water, using Pt/C catalysts. The primary hydroxyl group is preferentially oxidised using an unmodified catalyst. Addition of a lead(II)salt changes the preference dramatically towards oxidation at the position α to the carboxyl group. Study of the kinetics of the reactions is complicated by catalyst deactivation caused by as well oxygen as by (side)product adsorption. For the oxidation of D-gluconic acid to 2-keto-D-gluconic acid a dehydrogenation mechanism is proposed in which the α -H is activated by Pb^{II} -complexation of the carboxyl- and α -OH functions at the Pt-site.

INTRODUCTION

The oxidation of polyhydroxycompounds such as hexoses to polyhydroxycarbonic acids in aqueous solution by gaseous oxygen with the aid of noble metal catalysts has first been described by von Gorup-Besanz [1] in 1861 for the oxidation of mannose with platinum black. The hexose oxidation has been studied extensively by Heyns and coworkers [2-4], mainly using platinum on carbon as catalyst. Also de Wilt and van der Baan [5] and de Wit et al. [6] have contributed to this matter. In the patent literature we find a number of Japanese publications in which high yields of D-gluconic acid are obtained from D-glucose with the aid of palladium on carbon catalysts.

The drawback of these oxidations is that they do not stop at the hexonic acid stage but that a number of further oxidation products are formed. Poethke [7] reported that with a palladium catalysts D-gluconic acid yielded i.e., D-arabinonic acid and D-erythronic acid. De Wilt, Lindhout and Kuster [8-10], report on the kinetics of the formation of byproducts in the oxidation of D-glucose and D-fructose with platinum on carbon, and mention also D-glyceric acid, glycolic acid and formic acid. Mehlretter et al. [11] report D-glucaric acid as being the main product when D-gluconic acid is further oxidized with platinum catalyst. Dirkx et al. [12] have studied the latter reaction extensive-

ly. Due to the formation of other products the selectivity for D-glucaric acid was seldom above 60%. Obviously this rather low selectivity is caused by the fact that gluconic acid contains five hydroxyl groups, all of which are prone to further oxidation.

In an extensive study to improve the selectivity for D-glucaric acid we found, serendipitously, that modification of the platinum on carbon catalyst by lead compounds leads to a very selective formation of 2-keto-D-gluconic acid as we have already published elsewhere [13,14].

In this paper we present information regarding the reaction kinetics, the deactivation of the catalyst and the composition of the active ensemble for the selective oxidation on C_2 .

Flow sheet of the reactor and auxiliary equipment: 1, reactor; 2, turbine stirrer; 3, polarographic oxygen analyser; 4, thermostat; 5, drain; 6, sampling connection; 7, KOH burette; 8, substrate supply vessel; 9, condenser; 10, gas circulation pump; 11, pressure relief; 12, oxygen supply vessel; 13, gas burette; 14, contact manometer for pressure control.

SCHEME 1 Flow sheet of the reactor and auxiliary equipment.

EXPERIMENTAL

The preparation of the platinum on carbon catalysts and of the lead modified platinum on carbon catalysts have been described previously [13]. In general a 5% platinum on carbon catalyst is used on which lead (Pb^{2+}) is precipitated as $Pb(OH)_2$ or $Pb_3(PO_4)_2$ from a $Pb(OAc)_2$ solution with KOH or Na_3PO_4 . A lead platinum atomic ratio of 0.2 - 0.5 is used normally. The reactions are carried out in a stirred thermostatted sparged reactor (see scheme 1). The oxygen is circulated in a closed system through the reaction solution. A pressure

TABLE 1

Standard reaction conditions for the catalytic oxidation of D-gluconic acid and other substrates.

pH	8
T/°C	55
stirring rate/rpm	500
[substrate] ₀ /mmol l ⁻¹	200
%O ₂ in oxidation gas	100
catalyst Pb ₃ (PO ₄) ₂ /Pt/C/g l ⁻¹	40
Pb/Pt mol ratio	0.5

regulator admits fresh oxygen gas to this closed system to replace the oxygen consumed in the reaction. Due to oxidation generally more acids or more acidic products are formed and the pH is controlled at a constant level by adding KOH. Oxygen and KOH uptake are monitored. The standard conditions for the experiments are given in Table 1. Further experimental details have been given in a previous paper [13].

FIGURE 1 Main product distribution in the oxidation of D-gluconic acid with a standard Pb₃(PO₄)₂/Pt/C catalyst under standard conditions: ○ gluconic acid, □ 2-keto-D-gluconic acid, △ oxalic acid.

FIGURE 2 Main product distribution in the oxidation of D-gluconic acid with a Pt/C catalyst without Pb-additive under standard conditions: $\circ$ gluconic acid, $\triangle$ guluronic acid, $\square$ glucaric acid.

FIGURE 3 D-Gluconic acid concentration (logarithmic scale) as a function of time with the catalyst concentration as parameter at pH = 9, stirring rate 750 rpm, [catalyst]: $\triangle$ 40 g/l, $\square$ 20 g/l, $\diamond$ 10 g/l.

FIGURE 4 D-gluconic acid concentration after 300 seconds conversion as a function of the catalyst concentration.

FIGURE 5 D-gluconic acid concentration as a function of time with the oxygen partial pressure as parameter, stirring rate 320 rpm, ○ air, △ pure oxygen.

RESULTS AND DISCUSSION

Reaction kinetics

Under the experimental conditions of Table 1 the reaction proceeds as shown in Figure 1.

For comparison Figure 2 shows the product distribution as a function of time

when a standard platinum on carbon catalyst is used. The two figures demonstrate that the addition of lead phosphate to the platinum on carbon catalyst completely changes the main reaction route i.e., from oxidation on carbon atom number 6 with a Pt/C catalyst to oxidation on the second carbon atom with the lead modified Pt/C.

In Figure 3 the D-gluconic acid concentration is depicted as a function of time for three quantities of Pb/Pt/C catalyst. The reactions were carried out under standard conditions. A high stirring rate, 750 rpm, was used to prevent the oxygen transfer from the gas to the liquid to become rate determining. The pH was 9. We see that after an initially fast reaction the reaction rate decreases drastically. This deactivation makes the study of the intrinsic reaction kinetics rather complicated. Also the kinetic behaviour during the active period is uncommon. If we define the initial activity as being proportional to the quantity of D-gluconic acid converted in the first 300 s, this initial activity is directly proportional to the catalyst quantity as shown in Figure 4. On second thoughts this is a somewhat surprising result. According to the mass transfer rate equation $r = k_L \cdot a(C^* - C)$, the quantity, r , of oxygen transferred from the gas phase to the liquid (mol s^{-1}) is proportional to the difference between the equilibrium oxygen concentration in the liquid, C^* , about 0.9 mmol l^{-1} , and the actual concentration. Although our polarographic oxygen analyser was unable to cope with rapidly changing concentrations, we consistently found the oxygen concentration during the initial period of experiments with 40 g l^{-1} catalyst to be in the order of $0.001 \text{ mmol l}^{-1}$. Assuming that for the three experiments shown $k_L \cdot a$ is a constant, we calculate the oxygen concentration to be about 0.45 mmol l^{-1} during the initial period with 20 g l^{-1} catalyst and for the experiment with 10 g l^{-1} catalyst about 0.7 mmol l^{-1} . As we found (Figure 4) that the initial reaction rate was directly proportional to the catalyst quantity, we must conclude that the initial reaction rate is zero order in oxygen.

This suggests that, corresponding to what de Wit et al. [6,15] have shown for the oxidation of glucose, a hydrogen abstraction step to be rate determining in the oxidation of D-gluconic acid with a Pb/Pt/C catalyst.

At low stirring rates the oxygen transfer into the liquid becomes rate determining. In that case the initial reaction rate depends on the oxygen partial pressure in the gas phase. The experiments depicted in Figure 5 were done under low stirring rate conditions, and we see that the reaction rate with pure oxygen is about 5 times the rate found when air is used as the oxidizing gas. Under such conditions the reaction behaves as being first order in the oxygen pressure in the gas phase.

To investigate the order of the reaction in D-gluconic acid a series of experiments with a high stirring rate and a small quantity (5 g l^{-1}) of catalyst

FIGURE 6 D-gluconic acid concentration (logarithmic scale) as a function of time with the starting gluconate concentration as parameter, stirring rate 750 rpm, [catalyst] 5 g/l, [gluconic acid] at $t = 0$: $\diamond$ 400 mmol/l, $\circ$ 200 mmol/l, $\triangle$ 100 mmol/l.

and varying substrate quantities were executed. The results are given in Figure 6. We see that the active period is very short, but during that period always about 20% of the D-gluconic acid is converted. This is an indication that during the active period the reaction is first order in gluconic acid. Reverting to Figure 3 we see that after the initial period the logarithm of the concentration varies linearly with time, again indicating that the reaction rates are first order in the D-gluconic acid concentration. However, when we calculate the first order rate constant per gram of catalyst we find for the experiment with 40 g l^{-1} catalyst a rate constant that is 3.3 times the rate constant in the experiment with 20 g l^{-1} catalyst and 4.8 times the rate constant for the experiment with 10 g l^{-1} catalyst. This suggests that the catalytic activity in the reaction period under discussion is also influenced by another factor.

As for each of the three experiments the reaction rate constant remains constant during the whole reaction period it is rather unlikely that such changing factor as substrate or product concentrations are the cause of the differences in activity observed for the three runs. We revert to this subject in the next section.

FIGURE 7 Influence of the starting procedure on the oxidation rate of D-gluconic acid with a standard $Pb_3(PO_4)_2/Pt/C$ catalyst, stirring rate 500 rpm,

◇ starting procedure 0 , △ starting procedure N.

FIGURE 8 Influence of the starting procedure on the oxidation rate of D-gluconic acid with a 5% Pt/C catalyst [16], ○ starting procedure 0, △ starting procedure N.

The deactivation of the catalyst

Figures 1,3,5 and 6 show that the reaction rate decreases after an initial period of high activity. When we studied this phenomenon in more detail we found that the activity of the catalyst in the second period is influenced by the starting procedure used. We distinguish two starting procedures:

Starting procedure O:

The catalyst suspension and the concentrated substrate solution are heated to the reaction temperature in the oxidation gas atmosphere, and the experiment is started by introducing the concentrated substrate solution into the reactor.

Starting procedure N:

The catalyst suspension and the concentrated substrate solution are heated to the reaction temperature in a nitrogen atmosphere. After introducing the concentrated substrate solution into the reactor, the suspension is kept in a nitrogen atmosphere for 10 minutes. Thereafter the stirrer and the nitrogen flow are stopped. After the gas circulation system has been quickly evacuated and refilled with oxygen, the experiment is started by switching on the stirrer. Starting procedure N has been used normally in this study.

In Figure 7 we show the difference in activity resulting from the application of the two starting procedures for an oxidation reaction under standard conditions. Comparable, albeit less pronounced, differences have been reported by Dirkx and van der Baan [16] as shown in Figure 8 for the oxidation of gluconic acid with a platinum on carbon (Pt/C) catalyst. However, the behaviour of this catalyst and that of the lead modified platinum on carbon catalyst shows marked differences:

- the low activity of the Pt/C catalyst after starting procedure O can be restored to the level obtained by starting procedure N by simply substituting the oxygen by nitrogen for 600 s. This treatment has little effect with a Pb/Pt/C catalyst.
- the Pt/C catalyst shows a low activity with starting procedure O straight from the beginning of an experiment. The initial activity for the Pb/Pt/C catalyst is high. Independent of the starting procedure.

Dirkx and van der Baan [16] ascribe the deactivation of their catalyst to the action of oxygen on the catalyst. The two differences between the Pt/C and the Pb/Pt/C catalyst noted above show that for the deactivation of the latter catalyst oxygen is not the only factor.

To answer the question whether adsorption of certain reaction products or some other change of the catalyst is involved in the deactivation, we have re-used the catalyst and the reaction liquid resulting from an oxidation reaction in subsequent experiments according to scheme 2.

We used the standard conditions and a starting procedure which was modified as follows: instead of heating the catalyst suspension in the oxidation gas

SCHEME 2 Experimental set up to track down causes of catalyst deactivation.

atmosphere as in starting procedure 0, it was heated in a nitrogen atmosphere, and after the suspension had reached the operating temperature, it was treated with oxygen for 900 s.

In experiment 1 fresh catalyst and a fresh D-gluconic acid solution were used. After 650 s the catalyst was filtered off and washed with 3 l hot water to remove adsorbed reaction products as completely as possible. The filtrate was concentrated in a film evaporator at 50°C and D-gluconic acid was added to obtain again 0.5 l with a concentration of 200 mmol l⁻¹. Thereafter two experiments were carried out: the filtrate was contacted with fresh catalyst (experiment 2) and the used catalyst was contacted with a fresh D-gluconic acid solution (experiment 3).

For these three experiments the D-gluconic acid concentration as a function of time is given in Figure 9. Both experiments 2 and 3 show a lower reaction rate than experiment 1, but the reduction in activity is much greater in experiment 2 than in experiment 3. We therefore conclude that adsorption of reaction products also play a role in the deactivation of this catalyst.

The active ensemble

From previous experiments [18] we know that the Pt/C catalysts used have a high dispersion number (0.7 or higher). Nevertheless only a very small portion of the carbon surface, less than 0.5% is occupied by platinum. There is therefore ample room on the carbon to accommodate the lead compound on places isolated from the platinum.

That Pb₃(PO₄)₂ really interacts with the platinum of the catalyst follows from the subsequent experiments:

On 20 g of carbon carrier 1 g of platinum was deposited according to the standard procedure [13]. An equal amount of carbon carrier was treated identically, except that no H₂PtCl₆ was added. On both carriers 0.69 g Pb₃(PO₄)₂ (Pb/Pt = 0.5) was deposited in the usual way [13]. When both lead containing

FIGURE 9 Influence of re-use of catalyst and reaction mixture on the oxidation rate of D-gluconic acid with a standard $\text{Pb}_3(\text{PO}_4)_2/\text{Pt}/\text{C}$ catalyst, stirring rate 500 rpm, exp.1: Δ fresh catalyst + fresh gluconate solution, exp. 2: $\circ$ fresh catalyst + filtrate of experiment 1, exp. 3: $\diamond$ used catalyst + fresh gluconate solution.

products were exposed for 10 min. at 55°C to half a liter of a 200 mmol l^{-1} gluconic acid solution at pH 8 in a nitrogen atmosphere, we found the lead concentration in the solution contacted with the Pt free $\text{Pb}_3(\text{PO}_4)_2/\text{C}$ product to be 1.5 mg l^{-1} , whereas for the $\text{Pb}_3(\text{PO}_4)_2/\text{Pt}$ catalyst the lead content was below the detection limit. This means that the catalytically active lead compound in the $\text{Pb}/\text{Pt}/\text{C}$ catalyst is closely associated with the platinum.

As the substrate must be activated and positioned in such a way in relation to the hydrogen abstracting platinum site of the catalyst that this abstraction occurs preferentially at the second carbon atom, we assume that this is caused by the specific interaction between the substrate and the lead of the catalyst system. The literature on the complexation of D-gluconic acid with bivalent lead yields the following information [19-24]:

When we use for gluconic acid the notation used in the literature, HGH_4 , (the first H referring to the carboxyl hydrogen and the other four H's to the hydrogens of the four secondary hydroxyl groups) we can present the complexes formed between Pb^{2+} and HGH_4 as varying from $[\text{Pb}(\text{GH}_4)]^+$ at low pH to a rather insoluble $\text{Pb}_2(\text{GH}_4)_2(\text{OH})_2$ compound at high pH. Even compounds like $[\text{Pb}_2(\text{GH}_2)_2]^{2-}$ and $[\text{Pb}(\text{GH}_2)(\text{OH})]^{2-}$ are described.

From the stability constants reported for the various lead complexes it can

SCHEME 3 Dissociation of gluconate (20).

SCHEME 4 Lead gluconate (complex).

SCHEME 5 Mechanism of galactose dehydrogenation (15).

be calculated that under the conditions of our experiments, pH-9, lead(II) complexation with gluconate is more likely than with the hydroxyl ion.

Brannan and Sawyer [25,26] claim, on basis of unpublished NMR data, that in neutral solution the lead is bonded to the carboxylate group and the α -oxygen. They have demonstrated that in alkaline medium (pH 11-13) also the γ -oxygen is involved. Isbell's [27] optical rotation measurements and Melson and Pickering's [24] infrared data in combination with Littleton's [28] X-ray data of the lead alkali salt of D-gluconic acid support the conclusion that the α -oxygen is bonded to the lead ion.

SCHEME 6 Gluconate dehydrogenation at a Pt/Pb-site.

Coccioli and Vicedomini [20] have determined the dissociation equilibria for the D-gluconate anion at 25°C in 1 M NaClO₄ solution as given in scheme 3.

The fact that, at a pH as low 10.5, the hydroxyl functions involved in complex formation already start to dissociate, indicates that complex formation facilitates this dissociation.

The information presented above can be accommodated by the following structure of a dissolved lead gluconate species, that could occur at our reaction conditions as given in scheme 4. Because of geometric limitations, such a 1:2 lead gluconate complex is rather unlikely at the catalyst surface, but one might expect an adsorbed species of a 1:1 lead gluconate ratio.

According to Heyns et al. [30] the oxidation reactions of sugars and sugar derivatives on Pt/C catalysts is a dehydrogenation reaction. This has been confirmed by de Wit et al. [6] who found that in an alkaline medium and in the absence of oxygen aldoses are, in the presence of noble metals, converted to their aldonic acids with a concomitant production of hydrogen gas. They have also shown [15] that this dehydrogenation reaction can be depicted as given in scheme 5, and that for the reaction, proceeding via the glucose anion, the rupture of the carbon-hydrogen bond on C₁ is the rate-determining step.

In the molecular model of the active ensemble, shown in scheme 6, we suggest that, in analogy with the model of de Wit [31] in our case gluconate can form a complex with the lead in such a way that the hydrogen on C₂ is located favourably for abstraction. Moreover, the coordination with Pb(II) can be considered to enhance the ability of the hydrogen at C₂ to be transferred as a hydride ion.

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