Effect of pH in the Pt-catalyzed oxidation of D-glucose to D-gluconic acid

A. Abbadi *, H. van Bekkum

Delft University of Technology, Laboratory of Organic Chemistry and Catalysis, Julianalaan 136, 2628 BL Delft, Netherlands

Abstract

The pH effect on the Pt-catalyzed selective heterogeneous oxidation of D-glucose to D-gluconic acid was studied. The oxidation reactions were performed in the pH range 2 to 9 in a batch reactor using 5% Pt/C as the catalyst while monitoring the progress of the oxidation reaction. Accurate analysis of all products is offered. Inhibition of the catalytic activity was observed in acidic medium. The nature of the poisoning species is discussed taking into account the results obtained from electrocatalytic studies. Probably D-gluconic acid formed during the oxidation reaction is responsible for the poisoning of the catalyst. When adding bismuth as a promotor, the consecutive reaction towards 2-D-ketogluconic acid takes place and the poisoning in acidic medium is much less pronounced.

1. Introduction

Carbohydrates are an important class of renewable raw materials. Their oxidation can provide new compounds and materials with interesting physicochemical properties. Biocatalytic, stoichiometric chemical as well as homogeneous and heterogeneous chemocatalytic methods have been applied for the oxidation of sugar molecules. Several reviews dealing with carbohydrate oxidation have appeared [1–4].

The heterogeneous catalytic oxidations are mainly performed with air or oxygen in aqueous medium and in the presence of a supported noble metal catalyst. Heyns and coworkers have reviewed the reactivity toward oxidation of different functional groups of the carbohydrate molecules when using catalysts based on platinum in weakly alkaline medium [5,6]. In this way, the catalytic oxidation of D-glucose to D-gluconic acid using 5% platinum on charcoal was reported to provide good yield as well as selectivity when the reaction was carried out at pH = 8–9 [7–12]. Details related to the kinetics of the reaction were reported by de Wilt et al. [13]. Recently, Pd-based bimetallic catalysts were shown to be of advantage [14,15]. However, more information on the influence of different parameters such as pH, temperature and the presence of promotor on the course of the oxidation reaction is still needed to understand the behavior of the noble metal catalysts. The present paper deals with the pH effect on the platinum-catalyzed selective oxidation of D-glucose to D-gluconic acid. The pH range 2–9 was scanned by monitoring the conversion in a batch

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* Corresponding author.

reactor. 5% platinum on charcoal was used as the catalyst. The application of low pH would be of interest in developing a direct process from starch to gluconic acid, combining hydrolysis and oxidation. The influence of a bismuth promotor on the activity and the selectivity of the catalyst in acidic medium was also examined.

2. Experimental

2.1. Materials

D-Glucose was purchased from Merck and was used without further purification. The 5% platinum on charcoal (platinum dispersion 0.51, as determined by CO adsorption) and 5% bismuth/ 5% platinum on charcoal (platinum dispersion 0.24) were obtained from Degussa.

2.2. Oxidation equipment

Experiments were performed in a thermostatted glass batch reactor of 300 ml, equipped with a glass gas tight stirrer (1500 rpm). The pH was kept constant by using a pH meter (Metrohm 654) coupled to a pH control unit (Metrohm 614) and an automatic burette (Metrohm 655, 10 ml piston) containing 1.60 M KOH. The oxygen partial pressure of the gas phase could be adjusted to any desired value between 0.05 and 1 atm, and was kept constant during the reaction using an automatic oxygen supply system. This system consisted of a motor burette filled with water as displacing liquid, a thermostatted (30°C) gas burette filled with oxygen, and a differential pressure sensor, which operated the motor burette. Oxygen and hydroxide uptakes were recorded during the reactions. Further details related to the oxidation equipment were reported elsewhere [16].

2.3. Oxidation procedure

Reduction of the catalyst: required amount of powdered catalyst (0.04 g) was first introduced into the reactor, 50 ml of water was added and the system was flushed with nitrogen for 5 min to remove oxygen from the reactor. Then hydrogen was bubbled through the reactor for 5 min at a high flow rate and low stirring speed, and then for an additional 25 min at a low flow rate and high stirring speed. Finally, the hydrogen was removed from the gas phase by flushing with nitrogen for 5 min.

Starting up of the reaction: a defined amount of D-glucose (0.72 g) was dissolved in 30 ml of water and the solution was added to the suspended reduced catalyst under low nitrogen flow. The system was equilibrated at the preset temperature, and the desired oxygen partial pressure was set by sucking a calculated amount of gas out of the reactor, the gas being automatically replaced by pure oxygen. The reaction started immediately. The O_2 transfer was not the rate limiting step of the oxidation. The reaction was monitored by taking samples at suitable intervals of time and analyzing these by HPLC.

2.4. HPLC analysis

The samples were analyzed using a Dionex CarboPac PA1 column, with a Dionex PED 1 pulsed electrochemical detector containing a gold electrode to which potentials of E_1 0.1, E_2 0.6, and E_3 −0.8 V were applied for durations of T_1 0.5, T_2 0.09, and T_3 0.07 s. Two Waters M6000-A HPLC pumps, coupled to a Waters M680 gradient controller were used to adjust the required solvent gradient. NaOH and anhydrous NaOAc were used to prepare eluents in water, which was filtered and degassed with helium prior to the addition of these compounds. All solvents were stored in closed, pressurized vessels with helium purging. Compositions of solvents A and B were as follows: solvent A = 0.1 M NaOH, solvent B = 0.1 M NaOH and 0.5 M NaOAc. The flow rate was set at 1 ml/min. The gradient used for the analysis was as follows: 100% solvent A was used for 10 min followed by a linear gradient to reach the eluent composition of 60% A and 40% B in 10 min, this composition was maintained for 10 min

then the eluent was returned to 100% A in 5 min according to a linear gradient. The chromatographic data were processed using a Spectra Physics SP4270 integrator. Also, a Phenomenex Rezex organic acid column (60°C, eluent 0.01 M aqueous trifluoroacetic acid at 0.6 ml/min) was used to estimate the concentrations of the degradation products.

3. Results and discussion

The effect of the pH on the oxidation of D-glucose to D-gluconic acid catalyzed by 5% Pt/C catalyst is presented in Fig. 1. At pH 9, 7 and 5 the pH was kept constant by adding KOH. The initial rate decreased by a factor of two when the oxidation was carried out in neutral medium instead of at pH = 9. Below pH = 7 poisoning of the catalyst was observed. When the oxidation reaction was performed without pH control, inhibition of the catalyst activity took place rapidly and the oxidation process seemed to stop immediately. The pH at the end of the reaction was about 2.6. At pH = 5 the reaction reached ≈ 27% conversion

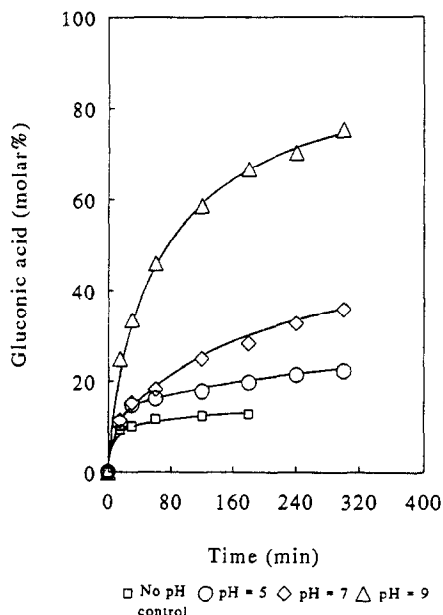Fig. 1. Effect of pH on the oxidation of D-glucose to D-gluconic acid. Glucose = 0.05 M (80 ml), catalyst = 0.5 g/l (5% Pt/C), T = 50°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

Table 1

Distribution of the main products (molar %) in the reaction mixture during the oxidation of D-glucose catalyzed by 5% Pt/C (reaction time = 6 h)

pH	G	GA (selectivity, %)	2kGA	GU	GR	AR	OX
9	15.1	75.4 (89)	0.3	4.2	1.2	0.6	4.5
7	54.7	35.9 (79)	2.0	2.2	0.4	0.7	3.9
5	72.3	22.3 (81)	1.0	0.7	–	0.4	3.7
No control	76.7	14.3 [a]	0.4	0.6	–	0.3	3.8

G = D-glucose, GA = D-gluconic acid, 2kGA = 2-keto-D-gluconic acid, GU = L-guluronic acid, GR = D-glucaric acid, AR = D-arabinonic acid, OX = oxalic acid. Glucose = 0.05 M (80 ml), catalyst = 0.5 g/l (5% Pt/C), T = 50°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

[a] Strong adsorption of reaction products on charcoal in acidic media does not allow accurate determination of the selectivity, however from the distribution of side products we can estimate the selectivity toward GA to be about 75%.

after 6 h reaction time. Thus the catalytic activity showed a strong dependence on the pH.

On the other hand, the variation in the pH of the oxidation reaction did not influence significantly the selectivity of the catalyst and the distribution of the main products (see Table 1, Scheme 1). Some 6-oxidation takes place as reflected by the presence of glucaric and guluronic acids and also some C–C splitting occurs, as was observed earlier in the oxidation of C_5 sugars (aldopentoses) [17]. The selectivity of the catalyst for the oxidation of D-glucose toward D-gluconic acid was reasonably good and ranged from 80% in acidic medium to almost 90% when the oxidation was carried out under alkaline conditions. The oxidation reaction was found to be first order in the catalyst. Strong adsorption of the reaction products on charcoal was observed when the oxidation was performed without pH control of the reaction.

As to the poisoning of the catalyst in acidic medium, two hypotheses could be formulated to explain the inhibition of the catalyst activity when the oxidation reaction was performed without pH control:

(i) Poisoning of the catalyst by oxygen. The noble metal becomes covered by chemisorbed oxygen and subsequently an amorphous oxide layer appears at the surface of the metal and the catalyst loses its activity. The phenomenon is
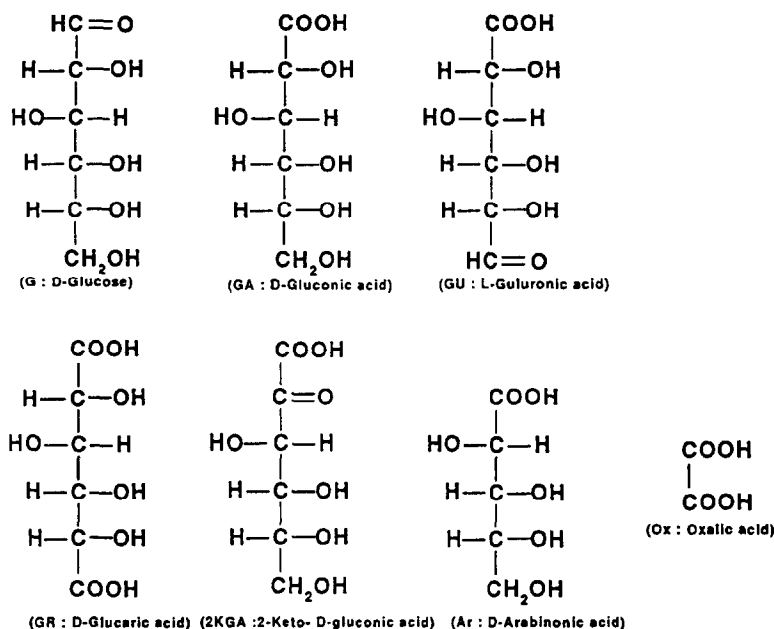
Scheme 1. Chemical formulae of the main products formed during the oxidation of D-glucose on Pt/C catalyst.

reversible in the sense that the catalyst can be reactivated by hydrogen or another reducing agent (formaldehyde, glucose).

(ii) Inhibition of the catalyst activity due to strong interaction of the active sites with the reaction products in acid medium. CO could be formed under these conditions which will adsorb selectively to the Pt surface. The following experiments have been performed to distinguish between (i) and (ii).

3.1. Reactivation of the catalyst by reduction with H_2

The oxidation reaction was run for 3 h without pH control. The poisoning of the catalyst took place within the first 1 h, afterwards no significant oxidation was observed. Reactivation of the catalyst by reduction was attempted as follows: the reaction system was flushed with nitrogen for 5 min to remove oxygen from the reactor, then hydrogen was bubbled through the reactor for 30 min and the system was flushed with nitrogen for 5 min. Upon replacing the gas phase by pure oxygen to restart the reaction, the oxidation did not proceed (see Fig. 2). This result is inconsistent with the first hypothesis; when the poisoning of

the catalyst is due to the formation of an oxide layer at the surface of the noble metal, reduction by hydrogen should restore the catalytic activity.

3.2. Reactivation of the catalyst by raising the pH to 9

The oxidation reaction was run until the inhibition state was reached. After 3 h, the catalyst was reactivated by adding a solution of KOH to the reaction mixture until pH 9 was attained. The pH was further kept constant in the usual way after reactivation. The reaction restarted immediately and the remaining glucose was further oxidized (Fig. 3). This result is in agreement with the second hypothesis. Since the selectivity towards D-gluconic acid is very high at the beginning of the reaction, we assume that this compound constitutes the main poisoning species. Earlier we reported on a similar poisoning effect on Pd/C as catalyst during the oxidation of D-glucose in acidic medium (reaction carried out without pH control) [18]. The 'free' carboxyl group of D-gluconic acid, the only reaction product formed according to HPLC, was considered to be responsible of the poisoning of the active sites of the noble metal catalyst. Also, electrocatalytic oxidation of D-glu-
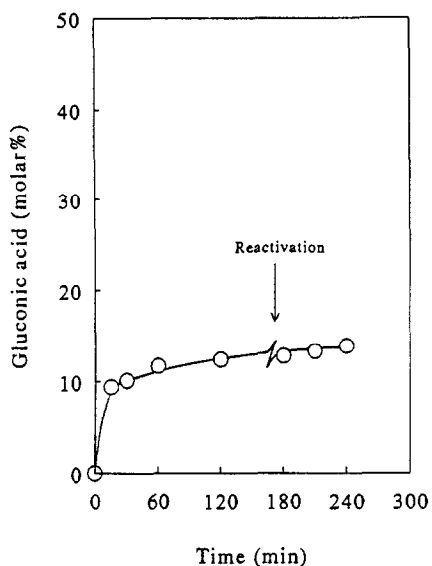
Fig. 2. Attempted reactivation of the catalyst in acidic medium by reduction with H_2. Glucose = 0.05 M (80 ml), catalyst = 0.5 g/l (5% Pt/C), without pH control, $T = 50°C, p(O_2) = 0.2$ atm, p(total) = 1.0 atm.

cose on a palladium electrode was found to suffer from the poisoning by 'free' gluconic acid [18]. However in the electrocatalytic literature, poisoning of platinum electrodes is generally attributed to adsorbed CO_{ad}. Most experimental evidence is based on the oxidation of methanol [19,20]. The initial poisoning species in the case of the oxidation of methanol were adsorbed CHO_{ad} which was supposed to be transformed to adsorbed CO_{ad} [20]. In the case of the oxidation of glucose on a platinum electrode in acidic medium, CO_{ad} was detected as the major poisoning species [21–24]. However, the observation of CO_{ad} by spectroscopic methods is much easier than unambiguous identification of other complicated species such as D-gluconic acid. The adsorbed CO_{ad} observed is resulting from C–C bond breaking due to degradation of D-gluconic acid to a lower aldonic acid. Indeed, some arabinonic acid (< 1%) was formed (Table 1).

With the aim to check any poisoning of the catalyst (5% Pt/C) by adsorbed CO_{ad}, we have carried out the following experiment. The catalyst was reduced by hydrogen at room temperature in the usual way (see Experimental – Oxidation procedure) and the reactor was flushed with nitrogen,

then CO was conducted through the reactor for 30 min. Finally, the reactor was flushed with nitrogen and the substrate (glucose) was added to the CO-treated catalyst. The system was equilibrated at the pre-set temperature (50°C) and the gas phase was replaced by oxygen to start the oxidation. The reaction was performed without pH control because under these conditions the poisoning of the catalyst was observed.

We could notice that treatment of the catalyst by CO did not inhibit its catalytic activity and oxidation of glucose took place in the reactor. The conversion of glucose reached ≈ 16% after one hour. This result indicates that CO is not the poisoning species of the Pt catalyst under acidic conditions.

However, when Pt catalyst was brought in contact with gluconic acid before adding glucose to the reaction mixture, inhibition of the oxidation process was observed (glucose conversion after 1 h ≈ 5%). The above experiments leave 'free gluconic acid' as the poisoning species. Adsorption might be as such or as proton and carboxylate. In both cases raising the pH will induce the formation of dissolved carboxylate (gluconate).
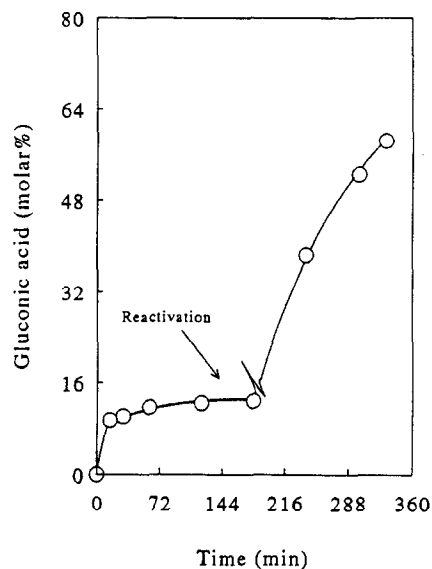

Fig. 3. Oxidation of glucose without pH control; reactivation of the catalyst by raising the pH to 9. Glucose = 0.05 M (80 ml), catalyst = 0.5 g/l (5% Pt/C), $T = 50°C, p(O_2) = 0.2$ atm, p(total) = 1.0 atm.
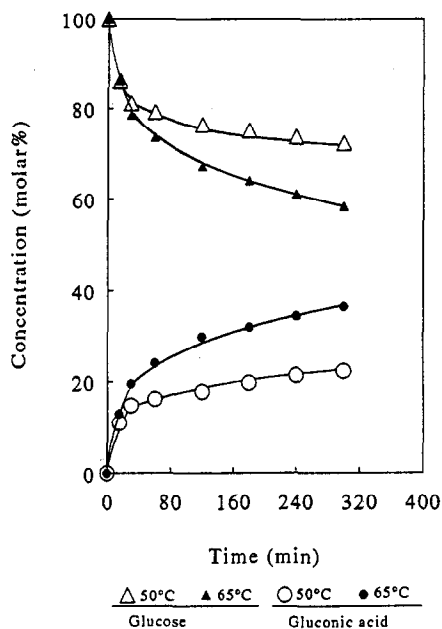
Fig. 4. Effect of the temperature on the oxidation of D-glucose to D-gluconic acid. Glucose = 0.05 M (80 ml), catalyst = 0.5 g/l (5% Pt/C), pH = 5, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

3.3. Effect of the temperature on the oxidation reaction in acidic media

An increase of the temperature from 50°C to 65°C did not greatly influence the initial rate of the oxidation reaction or the selectivity of the catalyst. The distribution of side products was comparable in both reactions. However, inhibition of the catalyst activity seemed to be delayed at 65°C and the oxidation reaction proceeded to a greater extent (Fig. 4). This is in harmony with the weaker adsorption at 65°C of the poisoning species (presumably gluconic acid) on the active sites of the noble metal.

3.4. Effect of a Bi promotor on the oxidation reaction in acidic media

The presence of a promotor as lead or bismuth beside platinum during the oxidation of glucose in weakly alkaline media was described in the literature [25,26]. The selectivity of the catalyst was directed to the oxidation of the anomeric carbon followed by the oxidation of the secondary hydroxyl group at the α-position of the newly

formed carboxylate function leading to the formation of 2-ketogluconic acid. In our case, we were interested in the effect of the promotor in the oxidation of D-glucose without pH control of the reaction. For this purpose, the amount of catalyst used was calculated on the base of the dispersion of platinum on the carrier as determined by CO adsorption. When using only platinum to perform the oxidation of D-glucose, without pH control of the reaction, inhibition of the catalytic activity was observed and the conversion was very low (≈ 22%). The presence of bismuth as promotor (in 1:1 wt ratio to Pt) led to interesting results. Not only the selectivity towards 2-ketogluconic acid was preserved, but also the inhibition of the activity of the catalyst in acidic medium was suppressed (Fig. 5). A similar effect on poisoning of platinum catalyst by bismuth promotion has been found during the oxidation of secondary alcohols such as 1-phenylethanol or diphenyl carbinol [27]. From our results we notice that the promotor (bismuth) fulfils two functions:

(i) Generation of the selectivity in the oxidation of the in situ formed D-gluconic acid toward 2-ketogluconic acid. This is explained in the lit-
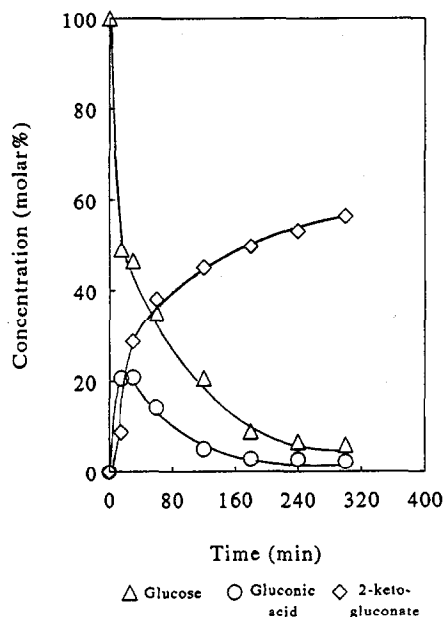

Fig. 5. Effect of promotor 'bismuth' on the oxidation of glucose without pH control. Glucose = 0.05 M (80 ml), catalyst = 6.55 g/l (5% Bi/ 5% Pt/C), T = 65°C, $p(O_2)$ = 0.2 atm, p(total) = 1.0 atm.

erature by assuming formation of a chelate complex between D-gluconic acid and the promotor involving the carboxylate and the 2-OH group [25,26]. In this way the 2-CH bond will be activated for hydride transfer towards the Pt surface.

(ii) Apparently, geometric covering by bismuth of a substantial fraction of platinum active sites weakens the adsorption of D-gluconic acid onto the catalyst surface allowing the oxidation to proceed substantially further than in the absence of bismuth.

Analogously, suppression by bismuth of the poison formation during electrocatalytic oxidation of methanol on platinum electrode in acidic media was recently reported [28]. Here, the elimination of poisoning effect was found to depend linearly on the coverage of the platinum electrode with bismuth.

4. Conclusion

In conclusion, the pH has a profound effect in the platinum-catalyzed oxidation of glucose to gluconic acid. Poisoning of the catalyst by the reaction products in neutral and acidic medium was observed and the degree of the inhibition of the catalytic activity was pH dependent. D-Gluconic acid in its 'free' form is considered to be the main inhibiting species of the platinum catalyst during the oxidation of glucose in acidic medium. When the temperature was increased the inhibition effect was delayed. The presence of bismuth as promotor beside platinum suppressed the physical poisoning of the catalyst while promoting selective oxidation of the gluconic acid formed in situ to 2-ketogluconic acid.

Acknowledgements

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