

Deactivation of Platinum Catalysts by Oxygen

1. Kinetics of the Catalyst Deactivation

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A study has been made of the kinetics of deactivation of a commercial Pt/C catalyst being used in an aqueous slurry for the oxidation of D-gluconate to D-glucarate at 50°C. It appears that the deactivation of the catalyst is an independent process, governed by the coverage of the platinum surface by oxygen atoms. Under steady-state conditions an exponential decay is observed. A mathematical model is presented, based on the processes occurring at the platinum surface, which describes the experimental results very well. © 1988 Academic Press, Inc.

INTRODUCTION

Catalyst deactivation is an important problem, especially in the case of large-scale production. Well-known causes of catalyst deactivation are sintering, irreversible adsorption of (by-)products or impurities in the feed, and deposition of carbonaceous material on active sites. Irreversible catalyst deactivation is of particular importance in the case of the application of noble metal catalysts because of their high initial costs.

Platinum catalysts are often used both for hydrogenation/dehydrogenation reactions and for oxidation reactions. Important applications of platinum catalysts in the field of oxidation are the complete combustion of automotive exhaust gases (1) and the oxidation of ammonia (1, 2). The oxidation of alcohols (3-6), aldehydes (6, 7), and sugars (8-12) may serve as examples of platinum-catalyzed oxidation reactions in the liquid phase.

During these processes a strong deactivation of the platinum catalysts often occurs due to the presence of oxygen. Ostermaier *et al.* (2) noted a strong catalyst deactivation during the low-temperature

oxidation of ammonia with oxygen, while Amirnazmi and Boudart (13) also found a loss of catalyst activity during the decomposition of nitrogen oxide over Pt/Al₂O₃. Deactivation of platinum catalysts also occurs during oxidation processes in the liquid phase as observed for example by Khan *et al.* in oxidizing ethylene glycol (3, 4) and Dirkx *et al.* in oxidizing D-glucose to D-glucarate (8-10). Also, patents have been published (14, 15) concerning the activity of platinum catalysts during oxidation processes in the liquid phase.

The oxidation of D-gluconate (obtained by oxidation of D-glucose) to D-glucarate involves a reaction intermediate, L-gulonate. The main reaction sequence is given in Fig. 1. The compounds D-gluconate and L-gulonate possess weak reducing properties. The overall selectivity to D-glucarate is about 50%. The remaining products are carboxylic acids of a lower molecular weight (as D-tartrate, tartronate, glycolate, D-erythronate, and oxalate) formed by C-C cleavage reactions on the catalyst surface. The main product of the oxidation reaction, D-glucarate, might be of commercial interest on account of its ability to form complexes with metal ions (16-18).

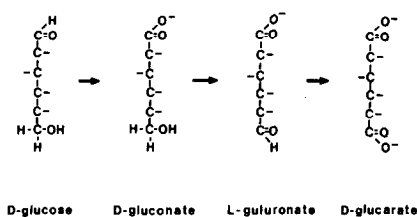


FIG. 1. Reaction sequence in the oxidation of D-glucose to disodium-D-glucarate.

A possible new application is the use of D-glucarate as a substitute for polyphosphates in detergents (19, 20).

A serious problem for the production of D-glucarate on a large scale is the rapid deactivation of the Pt/C catalyst under the reaction conditions used. An investigation on this subject has been started because information in the literature concerning this phenomenon is scarce. Special attention is given to the influence on the deactivation process of the oxygen pressure, D-gluconate concentration, pH, and temperature.

EXPERIMENTAL

The catalyst used in this study was commercially available 5% platinum on activated charcoal (Degussa F 196 RA/W). Other types of support were tested in the past but charcoal appeared to be preferable. The same conclusion was drawn by other authors oxidizing various alcohols under comparable reaction conditions (21, 22).

A first requisite to study catalyst deactivation is to maintain the reaction conditions at a constant level as a function of time. Batch experiments in which the deactivation proceeds along with conversion of D-gluconate cannot provide useful information on the factors which influence the deactivation process. Therefore an apparatus has been built (Fig. 2) to study the continuous oxidation of sodium-D-gluconate under steady-state conditions.

The main parts of the equipment are the reactor and the filtration vessel which are

kept at a constant temperature. A mixture of oxygen and nitrogen is supplied to the reactor containing the aqueous catalyst slurry. The concentration of oxygen in this slurry is measured with an oxygen probe (Ingold 533 sterilizable electrode) which displays the equivalent saturation pressure of the oxygen dissolved in the slurry. The oxygen pressure in the slurry, P_{O_2} , is controlled by a continuous adjustment of the stirrer speed. In this way a dynamic equilibrium is obtained between the amount of oxygen transferred from the gas phase to the slurry and the amount of oxygen consumed by reaction.

The pH of the slurry is kept at a constant level by titration with a solution of sodium hydroxide, in order to neutralize the sugar acids formed during the oxidation process. Simultaneously a solution of sodium-D-gluconate is added to the slurry in a constant proportion with the amount of alkali added (the production of 1 mole disodium-D-glucarate from sodium-D-gluconate requires 1 mole of alkali). The rate of deactivation of the catalyst is determined by recording the alkali consumption as a function of time. In this way the reaction conditions remain constant in time except for the catalyst

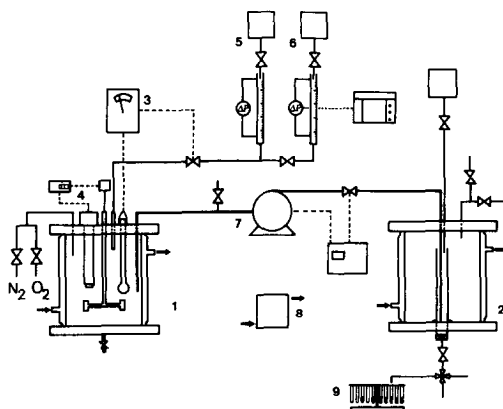


FIG. 2. Apparatus for continuous oxidation. (1) Reactor, (2) filtration vessel, (3) pH measurement/control, (4) measurement/control of partial pressure of oxygen in the liquid, (5) feed of alkali, (6) feed of sodium-D-gluconate, (7) pump, (8) thermostat, (9) sampling system.

concentration which slightly decreases by dilution with the solutions of alkali and sodium-D-gluconate. This is compensated by periodically pumping about 5% of the slurry to the filtration vessel followed by partial filtration. The resulting slurry is pumped back to the reactor. The filtrate is analyzed by high-speed liquid chromatography as described by Dijkgraaf *et al.* (23).

All experiments were performed at a temperature of 50°C, a pH of 9, and a catalyst concentration of 10 kg/m³ unless mentioned otherwise. In all experiments the conversion of sodium-D-gluconate in the reactor was kept at the same low level of about 5%, to avoid the possible influence of by-products on the catalyst deactivation. The reactant concentration, the partial pressure of oxygen in the slurry, the pH, and the temperature were varied in order to investigate their influence on the kinetics of the catalyst deactivation.

For the determination of the rate of deactivation in the absence of D-gluconate a different apparatus has been used. For these experiments portions of fresh catalyst in water were exposed to oxygen for periods of varying length, at the same temperature and pH as those used in the other experiments. After such a period the initial rate of reaction was determined by a batch experiment oxidizing sodium-D-gluconate

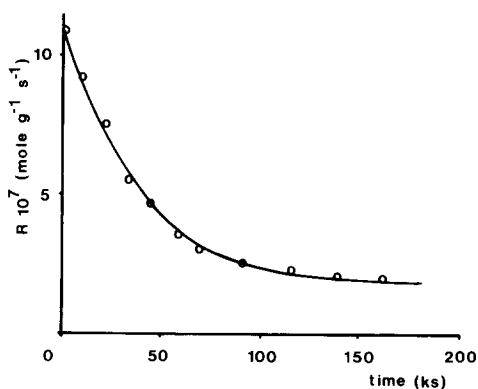


FIG. 3. Typical result of a deactivation experiment using a Pt/C catalyst for the oxidation of D-gluconate ($C_{GOZ,t=0} = 1.0 M$, $P_{O_2} = 1 \text{ bar}$).

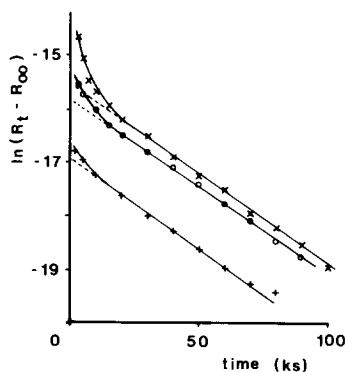


FIG. 4. Activity of the catalyst as a function of time and pH. (+) pH 7, (O) pH 8, (x) pH 9.

(0.5 mole/liter) in a slurry saturated with oxygen.

RESULTS AND DISCUSSION

Figure 3 illustrates a typical example of the deactivation of the catalyst in which the rate of reaction under constant reaction conditions is plotted as a function of time. Initially there is a fast deactivation of the catalyst, and after a long time a constant rate of reaction is obtained. By fitting the curves presented in Fig. 3 it appears that they can be described by the formula

$$R(t) = R_{\infty} + (R_0 - R_{\infty}) \exp(-K_D t). \quad (1)$$

In this formula R_0 and R_{∞} stand for the initial rate of reaction and the rate of reaction at infinite time, respectively, and K_D is the so-called deactivation constant which determines the rate of deactivation. K_D can be obtained from the slope of the plot of $\ln[R(t) - R_{\infty}]$ versus time.

In Fig. 4 the results are given in this way for three experiments carried out at different pH values. Dirks *et al.* (10) showed that the pH is an important parameter for the rate of reaction, and this is confirmed by the results in Fig. 4. However, Fig. 4 proves that the deactivation constant is hardly influenced by the pH. In Part 2 (24) it will be shown that the deactivation of

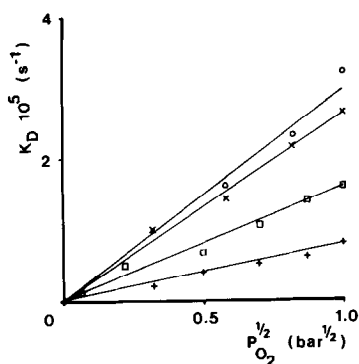


FIG. 5. Deactivation constant as a function of partial pressure of oxygen and sodium-D-gluconate concentration. Sodium-D-gluconate concentrations: (○) 0.25 mole/liter, (×) 0.5 mole/liter, (□) = 1.0 mole/liter, (+) 1.67 mole/liter.

platinum catalysts during the oxidation of D-gluconate can be ascribed entirely to the presence of oxygen. Series of experiments have been performed using a constant concentration of D-gluconate and different oxygen pressures. The deactivation constants belonging to these experiments are given in Fig. 5 as a function of the oxygen pressure and the D-gluconate concentration. It is striking that the deactivation constant depends on both parameters and decreases using a lower oxygen pressure or a higher D-gluconate concentration. From this result the assumption arises that the coverage of the platinum surface with oxygen is a predominant factor for the deactivation process. Lowering the oxygen pressure and increasing the D-gluconate concentration actually both decrease the part of the platinum surface which is covered by oxygen. This is also supported by the results in Fig. 4. Although the pH of this solution is of great importance for the rate of reaction (10) there is no relation between the pH applied and the deactivation constant. This confirms our assumption because the pH is only of minor influence on the part of the platinum surface covered by oxygen.

In the case of a deactivated catalyst the original rate of reaction may be restored by interruption of the oxygen supply to the

reactor or stopping the stirrer for a few minutes (the rate of deactivation of the catalyst after resuming the experiment, however, is higher (24)!). This reactivation is accomplished by reducing compounds in the reaction mixture which reactivate the deactivated platinum sites at the catalyst surface. Using a similar procedure, regeneration of a platinum catalyst was achieved in the case of the oxidation of other compounds such as ethylene glycol (3, 4), ammonia (2), and sugar acids (8–10). This regeneration process at the platinum surface will also occur during normal oxidation experiments. However, deactivation then dominates and the net result is a gradual decrease in the catalyst activity.

Equation (1) can also be derived starting from the three elementary processes that take place on the catalyst surface, namely, an oxidation, a deactivation, and a regeneration. Because of these general starting points the proposed model does not have to refer only to the oxidation of D-gluconate. It may possibly also hold for other oxidation processes using precious metal catalysts under comparable reaction conditions, during which (weak) reducing compounds are converted to their accessory products. The three elementary steps will now be discussed in some detail.

The oxidation reaction. As reported by Heyns *et al.* (25, 26) the reaction is initiated by an abstraction of a proton of a hydroxyl group of the sixth carbon atom in the chain by an OH^- ion, yielding water. After this step a hydride ion is transferred to the platinum surface giving the reaction intermediate, L-gulonate. An OH^- ion is obtained by reaction of the hydride ion with an adsorbed oxygen atom. The reaction path of the consecutive reaction of L-gulonate to D-glucarate proceeds in a similar way. It appears (27) that the rate of oxidation is proportional to the fractions of the platinum surface which are covered by oxygen, f_0 , and the organic reactant, f_A . If the oxidation reaction occurs only at the part of the catalyst surface which is still not deac-

tivated, $1 - x_i(t)$, the rate of oxidation is described by

$$r_{\text{ox}}(t) = k_{\text{ox}}f_A f_0(1 - x_i(t)). \quad (2)$$

The deactivation reaction. The deactivation of the catalyst is caused by dissociative chemisorption of oxygen followed by penetration of oxygen atoms into the platinum lattice. The nature of the deactivation is described in more detail in Part 2 (24). It is very likely that the rate of the deactivation reaction depends on the fraction of platinum sites at the surface which is not yet deactivated, $1 - x_i(t)$, and the fraction of sites which is covered with oxygen, f_0 :

$$r_d(t) = k_d f_0(1 - x_i(t)). \quad (3)$$

The regeneration reaction. The interaction between a reducing compound A and a deactivated site may result in a regeneration of this site. The rate of regeneration will probably depend on the fraction of platinum sites which are deactivated, $x_i(t)$, and the fraction of the surface covered by the reducing reactant, f_A :

$$r_r(t) = k_r f_A x_i(t). \quad (4)$$

As a first approach it is assumed that no difference exists between the adsorption equilibria of a reactant on active or deactivated platinum sites. As the reaction is performed under steady-state conditions (i.e., a constant composition of the reaction mixture) f_A and f_0 will remain constant in time.

The change of the amount of active platinum sites per unit of time is given by the difference of the rates of the deactivation reaction and the regeneration reaction:

$$\frac{Sdx_i}{dt} = (r_d - r_r). \quad (5)$$

Substitution of Eqs. (3) and (4) in (5) results after integration in

$$x_i(t) = x_{i,\infty} + (x_{i,0} - x_{i,\infty}) \exp(-K_D t) \quad (6)$$

in which $x_{i,\infty}$ is the deactivated fraction of

the platinum surface at infinite time and equals, $k_d f_0 / (k_d f_0 + k_r f_A)$, $x_{i,0}$ is the deactivated fraction of the platinum surface at $t = 0$, and K_D is the deactivation constant (s^{-1}) and equals $(k_d f_0 + k_r f_A) / S$.

Wolf and Petersen (28) derived a similar type of relation for a reaction with a self-poisoning parallel reaction due to an irreversible interaction of a reactant adsorbed on an active site. The introduction of a regeneration reaction as in our case, however, does not result in a greatly different expression.

The total rate of reaction is obtained by the summation of Eqs. (2) and (4). Equation (4) is included because the regeneration reaction also contributes to the conversion of the organic reactant into products:

$$R(t) = r_{\text{ox}}(t) + r_r(t). \quad (7)$$

$R(t)$ is also obtained by the multiplication of the initial rate of reaction, R_0 , and Eq. (6). In this way a relation similar to Eq. (1) is obtained. Thus the theoretical result fits the experimental results very well.

At the start of our deactivation experiments the catalyst deactivates faster than predicted by the theoretical model. Khan *et al.* (3) obtained curves similar to those in Fig. 4 when oxidizing ethylene glycol in an aqueous slurry of a Pt/C catalyst. Sárkány and Gonzalez (29) observed this phenomenon when oxidizing CO at low temperatures and explained it by a rapid adsorption of unreactive oxygen on Pt sites of low surface coordination. Until now, however, no satisfactory evidence was available for this assumption.

The rates of reaction attained are rather low. When D-glucose was oxidized, higher rates of reaction were obtained with respect to the oxidation rate when sodium-D-glucuronate was oxidized under the same reaction conditions. With regard to the molecular structure both compounds are rather similar. Accordingly, limitation of the rate of reaction by mass transfer of either reactant, D-gluconate or oxygen, from the aqueous phase to the catalyst surface is not

very likely. As regards the equilibrium condition for adsorption, it is very likely that the Langmuir theory is applicable.

The deactivation constant can now be written as

$$K_D = \frac{k_d f_0 + k_r f_A}{S}$$

$$= \frac{k_d (K_{O_2} C_{O_2})^{0.5} + k_r K_A C_A}{S(1 + (K_{O_2} C_{O_2})^{0.5} + K_A C_A + \sum K_x C_x)} \quad (8)$$

The oxygen concentration in the slurry is proportional to the partial pressure of oxygen in the reaction mixture (C_{O_2} may be obtained by multiplication of P_{O_2} with the Henry coefficient which is determined as a function of the concentration of several compounds). Hence the deactivation constant is proportional to $(P_{O_2})^{0.5}$ as long as it holds that

$$(K_{O_2} C_{O_2})^{0.5} \ll 1 + K_A C_A + \sum K_x C_x \quad (9)$$

According to the results in Fig. 5 it was found that a linear relationship exists between K_D and $(P_{O_2})^{0.5}$. Apparently the condition as given by Eq. (9) is fulfilled. In Fig. 5 the interception of all lines with the K_D axis is located in the origin. This means that the term $k_r f_A C_A$ in the numerator of Eq. (8) is very small compared to the other term

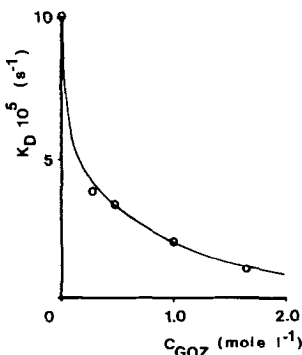


FIG. 6. Deactivation constant as a function of sodium-D-gluconate concentration ($P_{O_2} = 1$ bar).

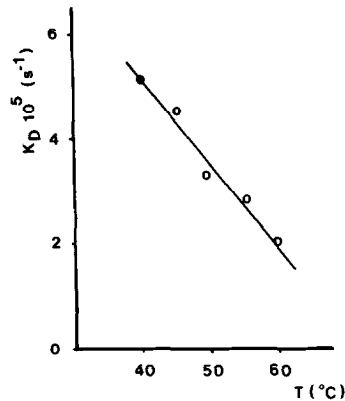


FIG. 7. Deactivation constant as a function of temperature ($P_{O_2} = 1$ bar, $C_{GOZ} = 0.5$ mole/liter).

$k_d (K_{O_2} C_{O_2})^{0.5}$. From Eqs. (3) and (4) it then follows that the regeneration reaction is much less significant than the deactivation reaction. All together K_D may be simplified to

$$K_D = \frac{k_d (K_{O_2} C_{O_2})^{0.5}}{S(1 + K_A C_A + \sum K_x C_x)} \quad (10)$$

From Eq. (9) it follows that the fraction of the platinum surface covered by oxygen atoms must be rather low. This means that in view of the high rates of deactivation of the catalyst observed during our experiments, the reaction rate constant k_d in Eq. (3) is quite high.

In Fig. 6 the deactivation constant is plotted as a function of the sodium-D-gluconate concentration (all these experiments were performed using a reaction mixture saturated with oxygen at 1 bar). The path of the curve corresponds with the general formula as given by Eq. (10). The deactivation constant at a zero concentration of D-gluconate in Fig. 6 was obtained by batch experiments as described under Experimental.

As illustrated in Fig. 7, the deactivation constant appears to decrease linearly with increasing temperature (all experiments were performed using a reaction mixture saturated with oxygen at 1 bar). Ostermaier *et al.* (2), studying the low-temperature

oxidation of NH_3 , also noted a decreasing extent of deactivation with increasing temperature. They ascribed this effect to an increasing reduction (regeneration) ability of NH_3 at elevated temperatures. It is difficult, however, to predict in the light of Eq. (10) what kind of relation exists between the deactivation constant and the temperature. All rates of reaction and adsorption equilibria presumably depend on the temperature to a different extent, while it is impossible to determine the influence of the temperature on all rate and adsorption constants.

APPENDIX: NOMENCLATURE

R	rate of reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
R_0	initial rate of reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
R_∞	rate of reaction at infinite time ($\text{mol g}^{-1} \text{s}^{-1}$)
K_D	deactivation constant (s^{-1})
t	time (s)
r_{ox}	rate of oxidation reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
k_{ox}	rate constant of oxidation reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
r_d	rate of deactivation reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
k_d	rate constant of the deactivation reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
r_r	rate of regeneration reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
k_r	rate constant of the regeneration reaction ($\text{mol g}^{-1} \text{s}^{-1}$)
S	total amount of platinum sites per gram of catalyst (mol g^{-1})
x_i	the inactive fraction of the platinum sites
f_i	fraction of the platinum surface covered by compound i
K_{O_2}, K_A, K_x	adsorption constants
P_{O_2}	partial oxygen pressure in the slurry

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