Deactivation of Platinum Catalysts by Oxygen

2. Nature of the Catalyst Deactivation

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The effect of different start-up procedures on the deactivation of a 5% Pt/C catalyst used for the oxidation of D-gluconate has been investigated. Results have been obtained both in a stirred tank reactor for batch experiments and in an apparatus for continuous oxidation processes. The deactivation of the catalyst is not explicable by formation of platinum oxides. A model is proposed for the deactivation of platinum catalysts by oxygen, based on penetration of oxygen atoms into the platinum lattice. © 1988 Academic Press, Inc.

INTRODUCTION

In Part 1 (preceding paper) (*1*) we reported on the deactivation of a Pt/C catalyst as observed during the oxidation of D-gluconate in an aqueous phase. In the literature, deactivation of platinum catalysts has been reported for oxidation processes of various compounds under various reaction conditions (*1–12*). However, there is no general agreement as to the cause of this deactivation. Sárkány and Gonzalez (*13*) and Cant (*14*) explained the catalyst deactivation observed during their oxidation experiments by the presence of chemisorbed unreactive oxygen atoms. Ostermaier *et al.* (*12*) observed a decline in the activity of a Pt/Al₂O₃ catalyst during the low-temperature oxidation of NH₃. They suggested that the catalyst deactivation is caused by the formation of platinum oxides, related to the rate of reaction. They explained this statement by the formation of heated platinum sites or sufficiently excited oxygen atoms, due to the heat of reaction, by which the formation of platinum oxides is initiated. Also Dirkx and van der Baan (*9, 10*) suggested a relation between the rate of reaction and the rate of deactivation of the Pt/C catalyst during the oxidation of D-glu-conate. They ascribed the catalyst deactivation to strong chemisorption of oxygen on platinum sites and formation of platinum oxides. Khan *et al.* (*4, 5*) attributed the deactivation of their Pt/C catalyst, used for the oxidation of ethylene glycol, to the formation of (unknown) oxidized platinum species combined with catalyst poisoning due to adsorption of by-products formed in the reaction.

Because there is no agreement in the literature on the cause of the catalyst deactivation during oxidation reactions under moderate reaction conditions, special attention has been paid to this subject in the present study. For this investigation use has been made of the platinum-catalyzed oxidation of D-gluconate to D-glucarate shown schematically in Fig. 1.

EXPERIMENTAL AND RESULTS

Batches of a fresh commercial 5% Pt on activated charcoal catalyst (Degussa F 196 RA/W) as delivered by the manufacturer were used throughout this study.

The experiments were performed in the stirred tank reactor illustrated in Fig 2. During the experiments a constant temperature and pH of the reaction mixture were maintained. The liquid was usually satu-
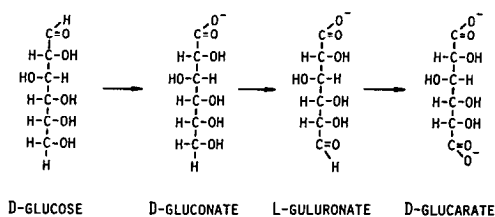
FIG. 1. Reaction scheme of the main oxidation reaction of D-glucose to disodium-D-glucarate.

rated with oxygen at a pressure, P_{O_2}, of 1 bar. The composition of the reaction mixture as a function of time was determined by high-speed liquid chromatography as described elsewhere (15).

Deactivation experiments were performed using a special apparatus designed

for continuous oxidation processes as described in Part 1 (1). Dirkx et al. (9–11) performed batchwise oxidation reactions of sodium-D-gluconate in a stirred tank reactor with a Pt/C catalyst prepared according to the procedure of Zelinskii. In their articles two different procedures are described to start the batchwise oxidation reactions:

Procedure A: The catalyst slurry is brought to the desired temperature and saturated with oxygen for a certain period. This is repeated with the solution of the reactant in a supply vessel. The reaction is started by adding the reactant solution to the catalyst slurry in the reactor.

Procedure B: The catalyst slurry in the reactor and the reactant solution in a supply vessel are brought to the desired temperature and saturated with nitrogen. After this, the reactant is added to the catalyst slurry in the reactor in a nitrogen atmosphere. After 10 min the reaction is started by replacing the nitrogen by oxygen.

In Fig. 3 the concentration of sodium-D-gluconate is plotted as a function of time for two experiments using procedures A and B. Our results are comparable to the results found by Dirkx et al. (9–11). It is interesting to compare these two experiments with a series of experiments using a fresh catalyst which was reduced with D-glucose for a long time (prereduction). The experiments
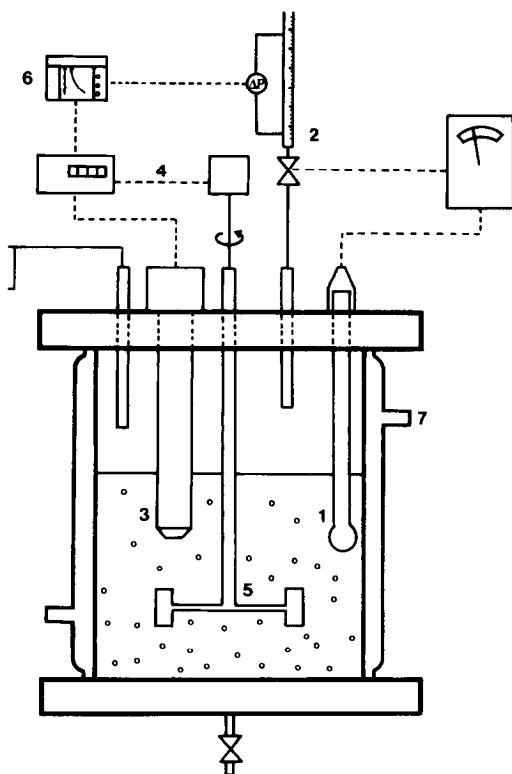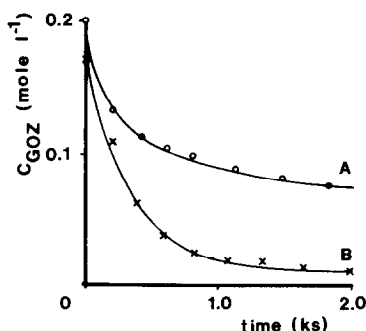

FIG. 2. Apparatus for batch oxidation of D-gluconate. (1) pH measurement, (2) pH control, (3) measurement of oxygen pressure in the reaction mixture, (4) control of stirrer speed, (5) stirrer, (6) recorder, (7) temperature control.

FIG. 3. Concentration of sodium-D-gluconate as a function of time for experiments performed with procedures A and B. $(C_{GOZ})_{t=0} = 0.2$ mole/liter, $C_{cat} = 4 \times 10^{-2}$ kg/liter, $T = 55°C$, pH 9.
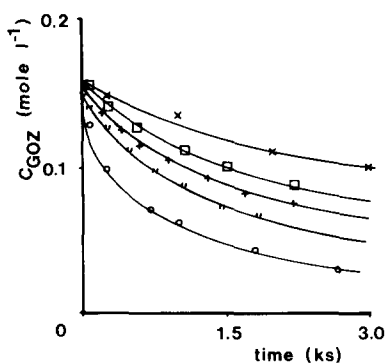
FIG. 4. Concentration of sodium-D-gluconate as a function of time for experiments performed with pretreated catalysts. Times of exposure of the reduced catalyst to oxygen: ($\bigcirc$) 0 s, ($''$) 150 s, ($+$) 300 s, ($\square$) 900 s, ($\times$) 25,000 s, $(C_{GOZ})_{t=0} = 0.175$ mole/liter, $C_{cat} = 4 \times 10^{-2}$ kg/liter, $T = 55°C$, pH 9.

of this series differ from each other by exposing the prereduced catalyst for different periods to oxygen in water under reaction conditions. The reaction is started using procedure C as described below. The results of these experiments are plotted in Fig. 4.

In this study two other (starting) procedures are used:

Procedure C: The catalyst is brought into the reactor under nitrogen. The reactant solution is separately brought to the desired temperature and saturated with oxygen. The experiment is started by adding the reactant solution to the catalyst and simultaneously replacing the nitrogen in the reactor by oxygen. In this way, the condition of the catalyst is not changed before the start of the experiment.

Procedure D: The experiment is started using procedure A and after a certain time the reaction is stopped by replacing the oxygen in the reactor by nitrogen or stopping the stirrer for several minutes.

The results using these procedures are plotted in Fig. 5.

Two experiments were carried out with another type of catalyst, i.e., the same catalyst in an oxidized form (Degussa F 196

N/W). One experiment was started using procedure B, applying a mixture of sugar acids as reactant, representing the products formed by the oxidation of D-gluconate. A second experiment was carried out with the same catalyst using D-gluconate and procedure B. In both cases no reaction occurred at all.

Finally, an experiment was performed using the apparatus for continuous oxidation processes as described in Part 1 (*1*). The experiment was started with a fresh catalyst. When the catalyst was strongly deactivated the stirrer was stopped for a couple of minutes during the experiment (to interrupt the oxygen transfer from the gaseous phase to the liquid) and restarted. A reactivation of the catalyst appeared, as shown in Fig. 6. Despite this regeneration period the activity fell back very quickly to the previous low level.

DISCUSSION

Catalyst deactivation is usually ascribed to sintering, irreversible adsorption of (by-) products or impurities in the feed, or deposition of carbonaceous material on active sites. From the results presented in Figs. 5 and 6 it appears that in the case of a deactivated catalyst as obtained during our oxidation experiments, the original rate of reaction may be regained by interruption of
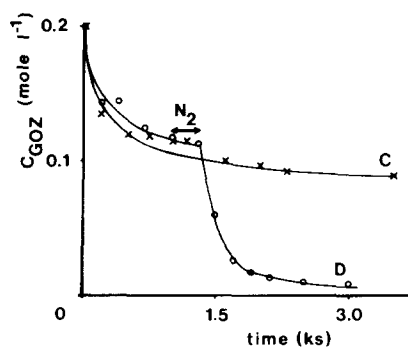

FIG. 5. Concentration of sodium-D-gluconate as a function of time for experiments performed with procedures C and D. $(C_{GOZ})_{t=0} = 0.2$ mole/liter, $C_{cat} = 4 \times 10^{-2}$ kg/liter, $T = 55°C$, pH 9.
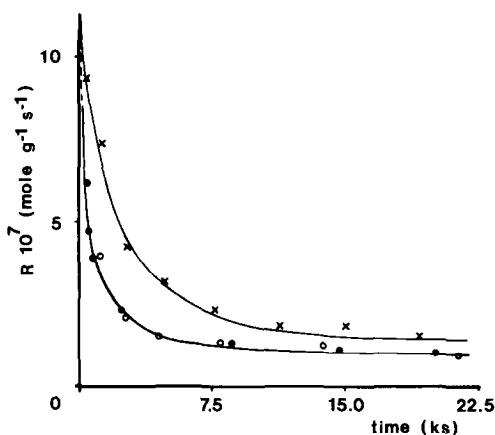
FIG. 6. Rate of the oxidation reaction as a function of time with interim regeneration of the catalyst: (×) fresh catalyst, (○) regeneration for 5 min, (●) regeneration for 40 min. Feed: 0.167 mole/liter of sodium-D-gluconate, conversion = 92%, $C_{cat} = 10^{-2}$ kg/liter, $T = 50°C$, pH 9.)

the oxygen supply to the reactor or by stopping the stirrer for a few minutes. Using a similar procedure, regeneration of a platinum catalyst was possible in the case of the oxidation of other compounds such as ethylene glycol (4, 5), ammonia (12), and sugar acids (1, 9–11). Because the initial rate of reaction of a regenerated catalyst was the same as that of a fresh catalyst, sintering or loss of platinum is excluded as an explanation for the observed catalyst deactivation. Furthermore, there is no reason why irreversibly adsorbed (by-)products, if present, should desorb from the catalyst surface by such a procedure. If the catalyst deactivation was caused by irreversible adsorption of (by-)products no regeneration of a deactivated catalyst would be expected. Although Khan et al. (4, 5) observed the same phenomena during ethylene glycol oxidation experiments they stated that the catalyst deactivation is partially caused by adsorption of by-products. As illustrated by the results in our preceding paper (Part 1) (1), the rate of deactivation decreases with increasing concentrations of organic reactant in the reactor. If (by-)products adsorb in an irreversible way

just the opposite effect should be expected because of a higher concentration of these products in the reaction mixture.

It turns out that by far the most important factor is the concentration of oxygen in the liquid. Accordingly, the catalyst deactivation is principally ascribed to the presence and action of oxygen.

Starting an experiment with procedure A leads to a less active catalyst with respect to an experiment performed using procedure B (Fig. 3). Dirkx et al. explained such results on the assumption that during an experiment started with procedure A the oxidation reactions become partly inhibited by chemisorbed oxygen on the platinum surface. However, it was observed during experiments conducted by one of us (16) that high initial rates occur at high oxygen concentrations in the liquid.

These results are in conflict with the suggestions of Dirkx and van der Baan (9, 10) for the rate differences observed for procedures A and B. Deactivation of a platinum catalyst merely by chemisorption of oxygen atoms on the platinum surface is therefore not very likely.

According to Dirkx and van der Baan (9) the deactivation of the catalyst is chemically coupled with the oxidation reaction. From the results of the experiments shown in Fig. 4 it is clear that the Pt/C catalyst deactivates also when it is exposed to oxygen in the absence of the other reactant, D-gluconate.

On the other hand, it appeared from the experiments described previously (1) that it is possible to oxidize considerable amounts of D-gluconate in a continuous reactor without an appreciable change of the catalyst activity over a long period by application of low oxygen concentrations in the liquid. Moreover, a change of the pH resulted in a change of the rate of reaction while there was no influence of the pH on the rate constant of deactivation of the Pt/C catalyst (1). Therefore it is concluded that the deactivation of the catalyst is not chemically coupled to the oxidation reaction.

The deactivation of the catalyst oxidizing D-gluconate can be described by a first-order process (1):

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

with $R(t)$ as the rate of reaction (mole s^{-1} g^{-1}), R_0 as the initial rate of reaction (mole $g^{-1} s^{-1}$), R_∞ as the rate of reaction at infinite time (mole $g^{-1} s^{-1}$), K_D as the deactivation constant (s^{-1}), and t as time (s). When an oxygen atom is situated on the platinum surface there are two possibilities: (i) the oxygen atom is used for the oxidation reaction; (ii) the oxygen atom starts to "react" with platinum, as a result of which the catalyst deactivation is caused. As stated previously (1), the deactivation constant depends on the fraction of the platinum surface which is covered by oxygen and factors which influence the "reaction" of oxygen atoms adsorbed on platinum atoms. This means that K_D in Eq. (1) depends on many (kinetic) parameters.

The Pt/C catalyst used (Degussa F 196 RA/W) was reduced by the manufacturer, and the catalyst was used approximately 1 year after delivery. When the results of the experiments performed with procedures B and C are compared with each other, the conclusion arises that the Pt/C catalyst deactivates during storage in air.

Ostermaier et al. (12) and Dirkx et al. (9–11) explained the deactivation of their catalysts (partly) by the formation of platinum oxides. They supposed that due to the chemical reaction a sufficiently excited oxygen atom or sufficient local heating is obtained to induce the platinum–oxygen reaction which yields platinum oxides. According to these authors this should result in a coupling between the rate of deactivation and the rate of oxidation. As explained earlier in this paper, however, this is not the case during our oxidation processes. Deactivation of platinum catalysts ascribed to the formation of platinum oxides was also reported by Amirnazmi and Boudart (3) during the decomposition of nitrogen oxide over Pt/Al$_2$O$_3$.

It is possible that PtO$_2$ is formed by local heating of platinum atoms during oxidation in the gaseous phase at elevated temperatures. This can hardly be the reason for deactivation of Pt/C catalyst during oxidation experiments in the aqueous phase (1, 4, 5, 9–11) because of the moderate conditions used.

It is shown that the catalyst also deactivates during storage. The formation of platinum oxides by local heat effects is not a plausible reason for the deactivation of the platinum catalysts in these circumstances, because no reaction is then going on.

From an experiment started with sodium-D-gluconate and using procedure D it appeared that the catalyst is reactivated by components in the reaction mixture during the period in which no oxygen is supplied (Fig. 5). Similar phenomena were observed by Ostermaier et al. (12) oxidizing ammonia with a Pt/Al$_2$O$_3$ catalyst. The strong deactivation of the catalyst during their experiments was also restored simply by temporarily stopping the oxygen flow. These regeneration effects were also found by Khan et al. (4, 5) during the oxidation of ethylene glycol in a weak alkaline slurry of a Pt/C catalyst. The same phenomenon was observed by Dirkx et al. (9–11).

To show that platinum oxides are probably not the cause of catalyst deactivation, comparative experiments have been performed with a Pt/C catalyst in an oxidized form, Degussa F 196 N/W, and a deactivated catalyst as obtained during our oxidation experiments. Although a reaction mixture is able to restore a deactivated catalyst (see the experiments mentioned above using procedures B and D) after which reaction takes place, no reaction occurred at all when starting with the catalyst in the oxidized form using procedure B. A similar phenomenon was noted in the case of the oxidation of aliphatic primary alcohols (17). A normal 10 wt% Pt/C catalyst could be used without pretreatment giving satisfactory results. PtO$_2$, however, needed to be

reduced by means of hydrogen, otherwise, no activity was obtained. Khan et al. (4) noted that a PtO_2/C catalyst could not be reduced to platinum by formalin treatment. Apparently the conditions of the surfaces of a deactivated catalyst and a catalyst in the oxidized form are not the same. From the experimental results it is not likely that the deactivation of catalyst is caused by formation of platinum oxides.

Mechanism of Deactivation

The platinum–oxygen system has been thoroughly studied in electrochemistry. A Pt electrode in 1 M H_2SO_4 saturated with oxygen in an open circuit has a surface coverage for oxygen atoms of approximately 0.3, while oxygen diffuses into the upper layers of the platinum lattice (18). Hoare et al. (19) showed that by the presence of oxygen in the platinum lattice an electrode material is generated with catalytic and electronic properties different from those of pure platinum. The dissolution of oxygen atoms into the platinum lattice (called "dermasorption") has also been established by Hoare (20) and Folguer et al. (21). Ratnasamy et al. (22) investigated supported platinum catalysts by the radial electron distribution (RED) technique. They concluded that a platinum particle after in situ reduction consists of unperturbed layers of Pt atoms ("bulk platinum") covered by two perturbed layers. Exposure of reduced catalysts to the atmosphere results in a complete disorder in these layers suggesting a 1 : 1 Pt : O stoichiometry. Stokes et al. (23) showed by NMR studies that each platinum site of a highly dispersed Pt/Al_2O_3 catalyst is bonded to six OH groups after exposure to air, while Pt–Pt bonds were no longer observed. Hoare (24) estimated by means of electrochemical experiments that a "saturated Pt–O alloy" should contain one O atom for every four Pt atoms. The same author (25), however, investigated such an alloy also by means of Auger electron spectroscopy (AES), X-ray photo electron spectroscopy (XPS), and scanning electron microscopy (SEM) and concluded that the Pt–O ratio in this alloy is lower than that stated above. Legare et al. (26), using XPS, showed the existence of subsurface oxygen, comparable to a "solution" of oxygen in the first layers of platinum. The oxygen atoms in the upper layers of platinum atoms are able to diffuse further into the platinum lattice by application of higher voltages during a longer period (20, 27, 28). In this way platinum oxides are also formed.

The observation that oxygen atoms dissolve into the platinum lattice instead of forming platinum oxides agrees with the findings of Boreskov (29) and Toyoshima and Somorjai (30). For most metals the initial heat of chemisorption coincides with the heat of formation of the higher oxides. For platinum, however, the heat of chemisorption of oxygen (71 kcal/mole) is notably higher than the heat of formation of platinum oxide, PtO_2 (32.2 kcal/mole). Supposing that the interaction between oxygen atoms and platinum atoms is similar for chemisorption of oxygen on platinum and dissolution of oxygen in platinum, it is clear that when platinum is contacted with oxygen, the oxygen atoms dissolve in the platinum lattice instead of forming platinum oxides.

Because of the findings of the authors mentioned above and our experimental results, a diffusion model is proposed to explain the deactivation of the platinum catalysts by oxygen. After the chemisorption of oxygen on the platinum surface, the oxygen atoms are able to diffuse into the platinum lattice. Dissolution of oxygen in the upper layers of metal atoms was also observed in the case of Pd catalysts (31, 32), even when conditions under which palladium oxide is unstable were used (33). By the interaction of the platinum lattice and oxygen atoms a solid phase which is unable to catalyze the desired oxidation of sodium-D-gluconate is formed. The catalyst can be reactivated by treatment of the catalyst with a reducing substance. This model also agrees with the
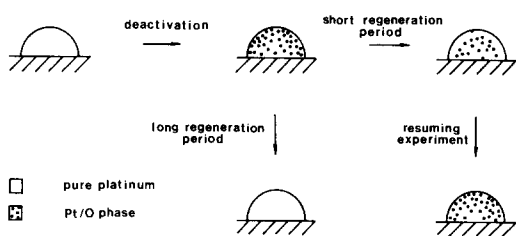
FIG. 7. Condition of a platinum particle during deactivation and regeneration periods.

experimental results of Dirkx et al. (9–11) and Khan et al. (4, 5).

This model also explains the results presented in Fig. 6 which were obtained in the apparatus used for continuous oxidation experiments. After reactivating the catalyst by replacement of oxygen by nitrogen for 5 or 40 min during the experiment, the catalyst deactivates very quickly when oxygen is brought in the reactor again. This might be explained by the assumption that during the regeneration period only the oxygen in the upper layer(s) of the platinum particles is removed. This may be due to the small diffusion coefficient of oxygen atoms in platinum (1.8–4.4×10^{-15} m^2/s) (34), or by the too low reducing power of the reducing compound. When the experiment is resumed the former condition of the catalyst will be restored very quickly. This process is sketched in Fig. 7. The small diffusion coefficient also explains why there is hardly any difference between the experiments after regeneration periods of 5 and 40 min. A complete regeneration of the catalyst apparently takes a long time. For Fig. 6 it follows that the initial rates of reaction in the case of a fresh catalyst and a regenerated catalyst are the same. This is more clear when the logarithm of the rate of reaction is plotted as a function of time (1). As shown in Fig. 7 a regenerated catalyst consists of a platinum–oxygen phase covered by a layer of only platinum atoms. This means that the underlying platinum–oxygen phase does not influence the rate of reaction, but merely acts as a buffer for ox-

ygen atoms which reenter into the first layer of platinum atoms, or catalyze rapid readsorption of oxygen in that layer.

ACKNOWLEDGMENTS

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