Chem. Pharm. Bull.
31(4)1141—1150(1983)

Liquid-Phase Oxidation of Ethylene Glycol on a Pt/C Catalyst. I. Deactivation and Regeneration of the Catalyst

MUHAMMAD ISHAQ ALI KHAN, YOSHIHISA MIWA,
SHUSHI MORITA, and JUTARO OKADA*

Faculty of Pharmaceutical Sciences, Kyoto University, Yoshida-Shimoadachi-cho, Sakyo-ku, Kyoto 606, Japan

(Received October 8, 1982)

Ethylene glycol was oxidized to glycolic acid in an alkaline solution over a Pt/C catalyst, and data were collected at 40°C and ambient pressure in a liquid-full reactor. During a run, strong catalyst deactivation took place, but could be partly reversed by temporarily stopping the reaction or treating the catalyst with formalin. The catalyst activity could also be restored (though not completely) by oxidizing the deactivated catalyst with oxygen, followed by reduction with hydrogen.

The deactivation of the catalyst is ascribed to the formation of some oxidized species (unknown) of platinum and/or to catalyst poisoning. The reactivation of the catalyst during the stopping period or on treatment with formalin is considered to be due to a reduction reaction between the oxidized species of Pt and ethylene glycol or formalin. The decay of catalyst activity is well described by a first-order deactivation process.

Keywords——ethylene glycol; liquid-phase; oxidation; platinum on carbon catalyst; deactivation; regeneration; liquid-full reactor

For the past few decades platinum-group metals have been commonly used for catalyzing the liquid-phase oxidation of alcohols and other related compounds in the pharmaceutical and chemical processing industries. A number of patents and papers[1-3] are available on this reaction system. However, the usual data reported are mainly concerned with conversions obtainable under different process conditions and with different catalysts, and little is known of the kinetics and mechanism of the reaction or of the mechanisms of catalyst deactivation and regeneration.

In our previous papers,[4,5] on the liquid-phase oxidation of diethanolamine by oxygen over Pd/Al_2O_3 catalyst, the kinetics and other mechanistic details were reported. The catalyst, when fresh, was found to exhibit a high activity, but was deactivated rapidly during the reaction. Moreover, the catalyst activity was found to decrease gradually when the catalyst was stored in a closed container under room conditions. Therefore, it is desirable to develop a relatively stable and active catalyst.

The present work is centered on the liquid-phase oxidation of ethylene glycol to glycolic acid by oxygen. Pt on carbon was used as a catalyst. Platinum supported on Al_2O_3 or C has commonly been used in heterogeneously catalyzed oxidations of various alcohols.[1,6-8] Carbon

TABLE I. Physical Properties of the Support

Surface area (N_2, BET method), m^2/g	950[a]
Pore volume, cm^3/g	0.991[b]
Solid phase density, g/cm^3	2.18[c]
Particle density, g/cm^3	0.69[b]
Bulk density, g/cm^3	0.382[b]
Porosity of particle	0.684[c]
Void fraction of bed	0.446[c]
Particle diameter, cm	0.055[d]

a) From Wako Chemical Industries. *b*) Measured.
c) Calculated. *d*) 28 to 32 mesh.

(granular) was used as a support because the active component (Pt) was well dispersed in it. The main purpose of this work was to study, (i) the various factors responsible for catalyst deactivation during the course of an experiment, and (ii) methods of regeneration of used (deactivated) catalyst. All experiments were performed in a liquid-full reactor, in which an oxygen-saturated alkaline solution of ethylene glycol was passed through a bed of catalyst particles. The above-mentioned topics are discussed on the basis of the global rate of oxygen consumption.

In the following paper,[9] the reaction kinetics and mechanism are discussed in detail.

Experimental

Chemicals——Reagent-grade ethylene glycol was used after distillation under reduced pressure (10 mmHg, 86°C). Reagent-grade hexachloroplatinic acid, sodium hydroxide (stated purity 95%) and formalin (37 wt%) were purchased from Wako Chemical Industries, Ltd. and used as supplied. Granular activated carbon (4—6 mesh) was used as a support. Commercial oxygen, nitrogen and hydrogen were used without further purification.

Catalyst Preparation——Granular activated carbon was crushed and sieved to obtain the 28 to 32 mesh fraction. To remove contaminating metals, the carbon particles were heated in 2 N hydrochloric acid solution at 80°C for 2 h. The carbon particles were washed with warm distilled water till the washings were Cl^--free ($AgNO_3$ test), then dried *in vacuo* and stored in a closed container under room conditions. The physical properties of the support are summarized in Table I.

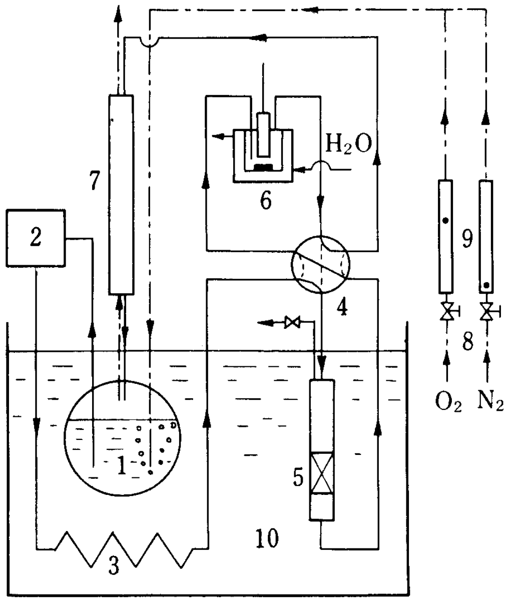

Fig. 1. Schematic Diagram of Reaction System

1, absorber; 2, quantitative pump; 3, preheater; 4, six-way valve; 5, liquid-full reactor; 6, oxygen analyzer; 7, packed bed (glass beads); 8, needle valve; 9, rotameter; 10, thermostat bath; ——→——, iquild flow line, ……→……, gas flow line.

(i) 0.1% Pt/C Catalyst: The catalyst was prepared by the method of Dirkx *et al.*[10] with some changes in the procedure.

An aqueous solution of a required amount of hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was added to a calculated quantity of the HCl-treated activated carbon particles. The adsorption of hexachloroplatinic acid on the support was carried out at 50°C and continued till the originally yellow solution became colorless. After standing overnight at room temperature, the adsorbed acid was reduced by slow addition of formalin (20 ml/g Pt) at pH 10.0 under room conditions over a period of 1 h. Then the catalyst suspension was heated to 80°C for 2 h. After standing overnight at room temperature, the catalyst was filtered off and washed with distilled water till the washings were neutral (litmus test). The catalyst was stored in distilled water under room conditions.

(ii) 0.12% PtO_2/C Catalyst: The catalyst was prepared by oxidizing the 0.1% Pt/C catalyst by passing oxygen continuously through the catalyst bed in a glass reactor at 300°C for 5 h.

Apparatus and Operating Procedure——Fig. 1 shows a schematic diagram of the apparatus used. The key parts are a liquid-full reactor 5 and an absorber 1.

In the absorber, 1.0 l of aqueous sodium hydroxide solution (0.1 M) was saturated with oxygen by continuous bubbling. The catalyst was packed in the glass reactor 5 (0.96 cm i.d. and 25 cm long). The catalyst particles were supported by a stainless steel screen (48 mesh) placed near the bottom of the reactor. The absorber and the reactor were placed in a thermostated bath 10, so that the reaction and absorption temperatures were equal. A series of runs was initiated by adding 0.1 mol of ethylene glycol to the absorber after treating the fresh catalyst (the procedure is described latter) with an oxygen-saturated alkaline solution. The mixture in the absorber was fed into the reactor by a quantitative pump 2. After passing through the reactor, the mixture was introduced into the top of a packed bed 7 (3 cm i.d. and 20 cm long) consisting of 3—4 mm glass beads. In this column the liquid was brought into contact with the gas stream leaving the absorber in a countercurrent mode, so that most of the oxygen consumed in the reactor was supplied from the flowing gas to the liquid. The liquid was then recycled through the absorber. The operating conditions are shown in Table II.

The oxygen concentrations in the liquid streams entering and leaving the reactor were measured with

TABLE II. Operating Conditions

Concentration of ethylene glycol, mol/cm^3	0.1×10^{-3}
Concentration of NaOH, mol/cm^3	0.1—0.3×10^{-3}
Concentration of oxygen in the liquid entering the reactor, C_{in}, mol/cm^3	0.96×10^{-6}
Liquid flow rate, Q_L, cm^3/s	0.23
Mass of catalyst in the reactor, m, g	0.46—0.80
Reaction temperature, °C	40.0
Total pressure, atm	1.0

an oxygen analyzer 6 (Toshiba-Beckman Model 777). The oxygen sensor was placed in a small water-jacketed glass vessel in which the liquid was continuously stirred. The global rate of oxygen consumption, R [mol/(g of catalyst)·s], was evaluated according to the following equation:

$$R = Q_L C_{in} X/m$$

where Q_L [cm^3/s] is the liquid flow rate, C_{in} [mol/cm^3] is the oxygen concentration in the liquid stream entering the reactor, m [g] is the packed mass of the catalyst, and x [−] is the oxygen conversion per pass.

Catalyst Pretreatment——Unless otherwise mentioned, prior to the reaction, the fresh catalyst was pretreated with oxygen in the following manner. Using the same apparatus (shown in Fig. 1), the alkaline solution saturated with oxygen in the absorber was fed repeatedly through the catalyst bed in the reactor and recycled to the absorber till the physical adsorption of dissolved oxygen in the solution on the catalyst surface had essentially reached completion (checked by means of the oxygen analyzer).

Catalyst Regeneration——Two methods were employed for regeneration of the catalyst.

(i) Formalin Treatment: The used (deactivated) catalyst was first thoroughly washed with warm distilled water to remove ethylene glycol and other reaction products. Thereafter, the catalyst was treated with a 3% formalin solution at 50°C and pH 12.0 for 4 h. To wash out the formalin, N_2-saturated alkaline solution was pumped through the reactor for 1 h.

(ii) Vapor-Phase Hydrogenation: A strongly deactivated Pt/C catalyst was first thoroughly washed with distilled water to remove the adsorbed substances as far as possible. The catalyst was dried *in vacuo* and then packed in a glass reactor. To remove the remaining adsorbed substances (poisons), first oxygen gas was passed through the catalyst bed at 300°C for 4 h, then oxygen was replaced by nitrogen gas and finally hydrogen gas was passed continuously for 5 h at the same temperature.

Results and Discussion

Repeated Use of Catalyst

Figure 2 gives the global rates of oxygen consumption as a function of time for a series of experiments (runs 21 to 27), where the same catalyst was repeatedly used. Hereinafter, each run is successively described.

Run 21——The fresh catalyst after treatment with nitrogen-saturated alkaline solution (20 h) was exposed to oxygen-saturated alkaline solution for 3 h. A marked decrease in the adsorption rate, shown by a curve in Fig. 2, suggests that oxygen adsorption on the catalyst surface was nearly in equilibrium.

Run 22——The reaction was started by feeding the oxygen-saturated reaction mixture and was continued for 4 h. From the data illustrated in the figure, a gradual decline in the catalyst activity with increasing reaction time can be seen. Since the initial concentration of ethylene glycol is about 100 times larger than the saturated concentration of oxygen (Table II) and the reaction is equimolar in them, the conversion of ethylene glycol per pass can be assumed to be negligible. Therefore, the concentration of ethylene glycol is considered to be uniform throughout the reaction system during a run. For example, for a supposed 20% average conversion of oxygen per pass, the conversion of ethylene glycol after 20 h of operation is calculated to be only 3.2%. Hence, the decrease in the reaction rate can be ascribed to the decrease in the number of active sites and/or to catalyst poisoning. The reaction system was left under room conditions for 64 h.

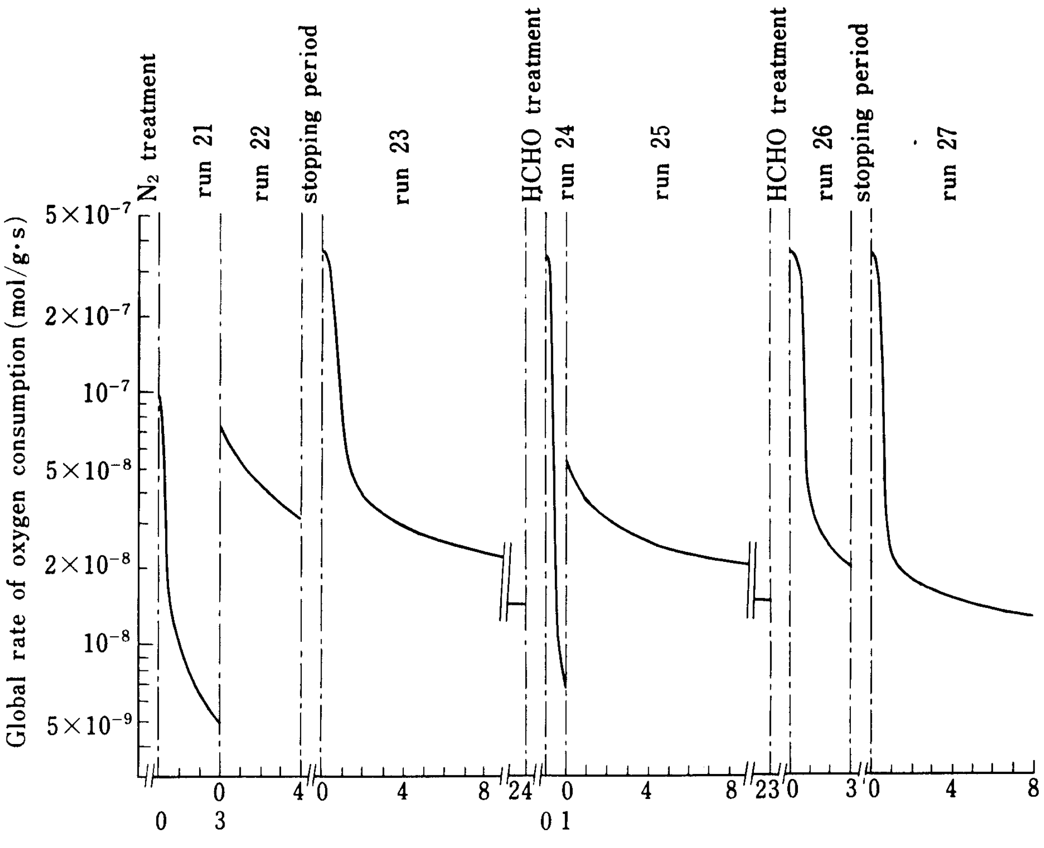

Fig. 2. Global Rates of Oxygen Consumption during Repeated Uses of the Catalyst

Run 23——The reaction was again started by feeding the oxygen-saturated reaction mixture from the previous run without pretreatment of catalyst with oxygen. The rate was very high ($x > 0.9$ and $R > 3 \times 10^{-7}$) initially, but decreased rapidly over the initial 2 h and then gradually in the same manner as in run 22. This behavior can be explained by assuming that during the stopping period, the oxygen dissolved in the bulk liquid as well as adsorbed on the catalyst surface is completely consumed by ethylene glycol, and as a result, in this oxygen-deficient state, the oxidized species of catalyst (deactivated catalyst) on reaction with ethylene glycol are reduced to more active platinum. To investigated this possibility further, the deactivated catalyst was treated with formalin solution.

Run 24——The formalin-treated catalyst was exposed to oxygen-saturated alkaline solution for 1 h. The adsorption rate of oxygen is much higher than that in run 21, particularly over the initial period. As the catalyst after preparation was stored in distilled water, some fraction of the active sites may be covered with oxygen dissolved in the water. The catalyst was treated with nitrogen prior to oxygen treatment. If the oxygen adsorbed on the catalyst surface was desorbed by nitrogen treatment, the rate pattern in the case of run 21 should have been nearly the same as that in the case of run 24. Thus, it can be concluded that under our experimental conditions, the nitrogen treatment of stored catalyst does not result in complete desorption of adsorbed oxygen. On the other hand, the deactivated catalyst on formalin treatment can be reduced to platinum. Hence, the amount of oxygen adsorbed per unit mass of catalyst (that is, $\int Rdt$) in the case of run 24 is greater than that in run 21 and adsorption of oxygen in both cases goes essentially to completion within 2 h. Further, the initial rate patterns for runs 23 and 24 are nearly the same. This indicates that at start of run 23 the catalyst is already in the reduced state. After an initial period (30 min), the rate of reaction in the case of run 23 is much higher than in run 24. As the rate in the case of run 24 corresponds to the adsorption of oxygen, the difference between the two rates is due to reaction. Hence, it can be concluded that the reduced catalyst exhibits very high activity. This catalyst hereafter is referred to as catalyst I.

It is important to note that the difference does not always correspond to the true rate of reaction. The reason is as follows. The intrinsic rate of this reaction was found to be independent of oxygen concentration[9] and calculation based on the Weisz criterion[11] reveals that under the present conditions all mass transfer resistances can be neglected when the global rate of reaction is below the order of 10^{-7} [mol/g·s]. In the case of $R > 10^{-7}$, the rate is mainly controlled by the liquid-solid and intraparticle mass transfer resistances, and the true of reaction is difficult to predict.

Run 25——This run was initiated in the same manner as run 22, and continued for 23 h. The rate pattern resembles that of run 22, though the initial rate for this run is lower than that for run 22. This difference can be ascribed to the irreversible poisoning of the catalyst and is discussed in detail later. The catalyst was once more treated with formalin.

Run 26——This run was started by feeding the fresh reaction mixture saturated with oxygen into the reactor containing the formalin-treated catalyst (from run 25). The catalyst was not pretreated with oxygen. After 3 h, the liquid feed was stopped and the reaction system was left as such under room conditions for 5 d.

Run 27——This run was started in the same manner as run 23. The rate pattern closely resembles those of runs 23 and 26, though the rate is somewhat lower.

Decay of Catalyst Activity

The experimental data depicted in Fig. 2 are replotted in Fig. 3 *versus* the time from the start of each run. We see that the global rate of oxygen consumption for the initial period (~1 h) for runs 23, 26 and 27, where the catalyst was not pretreated with oxygen, is much higher than that for runs 22 and 25, where the reaction was started with the oxygen-treated catalyst. The difference in the rates can be ascribed mainly to the rapid adsorption of oxygen on the catalyst surface and partly to the oxidation of ethylene glycol. The adsorption of oxygen on the catalyst surface goes essentially to completion within 2 h. After 2 h the rate curves are nearly parallel with each other, though the initial rate decreases with increasing run number. Moreover, the amount of oxygen consumed during the initial period in runs 23, 26 and 27 decreases with increasing run number. This suggests a decrease in the total number of effective active sites. As described in the preceding section, mass transfer effects are significant at global rates of reaction above the order of 10^{-7}, so that the true rate of reaction, or the true catalyst activity, is difficult to estimate. Thus, here the activity of catalyst I has not been taken into account.

The dotted curves in Fig. 3, drawn by extrapolating the rate data for runs 23, 26 and 27 after 2 h, may be regarded as the global rates of reaction which would have been observed with the oxygen-pretreated catalyst. Since the five curves, which are nearly parallel with each other, are in the reaction controlling regime, the corresponding rates of reaction represent the overall catalyst activity and the intercepts represent the activity of oxygen-pretreated catalyst. Hereafter, the active species of the oxygen-pretreated catalyst is referred to as II. Figure 4 gives the normalized global rates of reaction, R/R_0 [—], for all experimental data (6 different catalyst beds, 12 runs and 84 measurements; for runs 23, 26 and 27 the data in the initial 2 h are excluded) as a function of time. Here, R_0 [mol/g·s] is the initial rate of reaction for each run. On the whole, all the data points seem to be on one line which represents the changes in the overall activity during each run. We see a rapid decrease in the activity over the initial period. After 5 h the decline in the activity becomes gradual and linear. According to the general concept of catalyst decay,[12] the activity of a single active species may decline exponentially with time, *i.e.*, linearly on a semi-logarithmic plot. Thus, the decay pattern in Fig. 4 implies that the species II is rapidly transformed to a less active species which is poisoned slowly due to adsorption of reaction products as the reaction proceeds further.

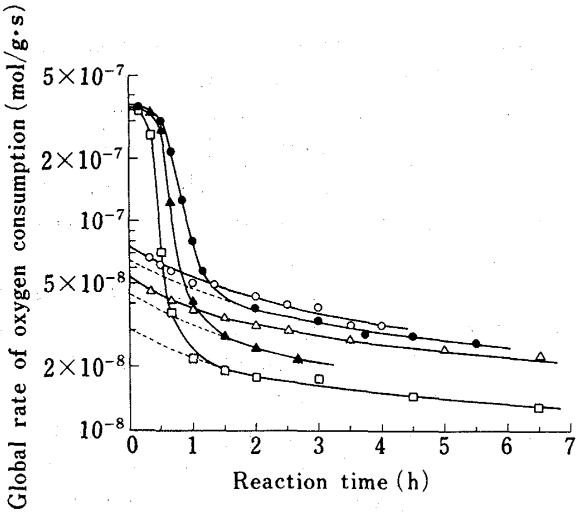

Fig. 3. Comparison of Global Rates of Oxygen Consumption

Concentration of ethylene glycol (mol/cm³), 0.1×10^{-3}; concentration of NaOH (mol/cm³), 0.1×10^{-3}; amount of catalyst (g), 0.61; ○, run 22; ●, run 23; △, run 25; ▲, run 26; □, run 27.

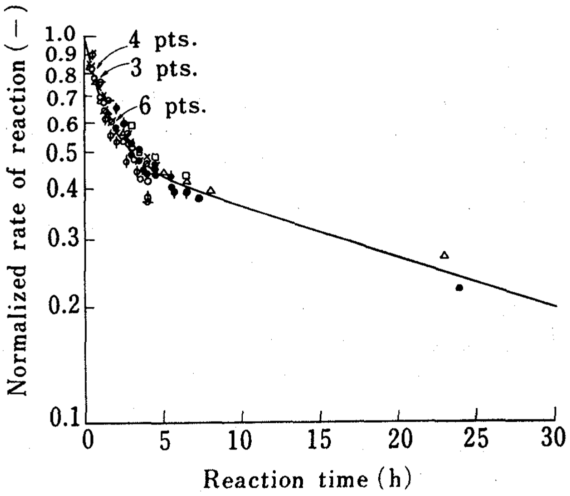

Fig. 4. Normalized Rate of Reaction *versus* Reaction Time

Concentration of ethylene glycol (mol/cm³), 0.1×10^{-3}; run no., concentration of NaOH (mol/cm³), amount of catalyst (g):
⊖, run 12, 0.1×10^{-3}, 0.46; -●-, run 13, 0.1×10^{-3}, 0.46;
○, run 22, 0.1×10^{-3}, 0.61; ●, run 23, 0.1×10^{-3}, 0.61;
△, run 25, 0.1×10^{-3}, 0.61; ▲, run 26, 0.1×10^{-3}, 0.61;
□, run 27, 0.1×10^{-3}, 0.61; ⦶, run 32, 0.1×10^{-3}, 0.76;
♦, run 33, 0.1×10^{-3}, 0.76; ×, run 42, 0.1×10^{-3}, 0.84;
∅, run 52, 0.2×10^{-3}, 0.80; ●, run 62, 0.3×10^{-3}, 0.80.

Somewhat analogous phenomena were observed by Dirkx *et al.*[10] in the oxidation of glucose with oxygen over Pt/C catalyst. In their case, a strong deactivation of the catalyst took place during the course of the experiment. Part of this catalyst deactivation could be reversed by temporarily stopping the oxygen flow (the oxygen effect), while another part could be reversed by washing the catalyst with hot distilled water (ascribed to the reversible adsorption of products). The deactivation was ascribed to the formation of platinum dioxide (PtO_2), which was supposed to be chemically coupled with the oxidation of glucose. The reactivation of catalyst in the absence of oxygen is reported to be a reduction reaction between PtO_2 and adsorbed glucose. Three different oxidized species of platinum, *i.e.*, (i) $Pt{\cdot}O_2$ (loosely bound oxygen), (ii) Pt–O (chemisorbed oxygen) and (iii) PtO_2, are reported to be involved in the reaction, though no details regarding the identifications are cited.

To check whether PtO_2 exhibits activity or not, we carried out an experiment with PtO_2/C catalyst. Under our experimental conditions this catalyst showed very little activity and could not be reduced to platinum by formalin treatment.

The species II is assumed to be $Pt{\cdot}O_2$, but it is uncertain that it may be transformed to Pt–O. However, the experimental results in Fig. 4 suggest that at least one more active species (different from II) is involved in the reaction. Hereafter this species with mild activity is referred to as III. It is evident from Fig. 3 that the number of effective active sites decreases

$$\underset{\substack{(\text{Pt})\\ \text{very high activity}}}{\text{catalyst I}} \xrightarrow{\text{oxygen treatment}} \underset{\substack{(\text{Pt}\cdot\text{O}_2)\\ \text{high activity}}}{\text{catalyst II}} \xrightarrow[k_2]{\text{reaction}}$$

$$\underset{\substack{(\text{some oxidized species})\\ \text{mild activity}}}{\text{catalyst III}} \xrightarrow[k_3]{} \underset{\substack{(\text{unknown})\\ \text{no activity}}}{\text{IV}}$$

Chart 1

slowly during the reaction due to the poisoning of the catalyst. An experiment carried out with a small quantity of glycolic acid (product) in the reaction mixture revealed that the rate of reaction is independent of the concentration of glycolic acid.9) Therefore, this poisoning is considered to be due to adsorption of some reaction by-products.

Based on the above-mentioned considerations and facts, we propose the following scheme for catalyst deactivation.

An inactive (deactivated) species referred to as IV is assumed to be formed from III. Supposing a first-order conversion for each active species involved in the reaction, the following rate equations can be formulated;

$$d\,[\mathrm{II}]\,/dt = -k_2[\mathrm{II}] \quad (1)$$

$$d\,[\mathrm{III}]\,/dt = k_2[\mathrm{II}] - k_3[\mathrm{III}] \quad (2)$$

with the initial condition;

$$t = 0\,;\ [\mathrm{II}] = 1 \text{ and } [\mathrm{III}] = 0 \quad (3)$$

where [II] and [III] are the relative concentrations of active sites, k_2 and k_3 [1/s] are the respective first-order rate constants and t [s] is the reaction time.

Integration of equations (1) and (2) with the initial conditions (3) gives the normalized rate as,

$$R/R_0 = K\exp(-k_2t) + (1-K)\exp(-k_3t) \quad (4)$$

with

$$K = 1 - \frac{k_2\ {}^{a}\mathrm{III}}{(k_2-k_3)^{a}\mathrm{II}} \quad (5)$$

where ^{a}II and ^{a}III [mol/g·s] are the activities of II and III, respectively. Using all the data represented in Fig. 4, a nonlinear least-squares analysis gives the values $K=0.51$ [—], $k_2=0.74$ [1/h] and $k_3=0.030$ [1/h]. The line on Fig. 4 was estimated by means of equation (4) with these values, and the activity ratio ${}^{a}\mathrm{III}/{}^{a}\mathrm{II}$ was estimated to be 0.47.

The total concentration of the active sites, [II]+[III], can be expressed as

$$[\mathrm{II}] + [\mathrm{III}] = K'\exp(-k_2t) + (1-K')\exp(-k_3t) \quad (6)$$

where

$$K' = 1 - \frac{k_2}{k_2-k_3} \quad (7)$$

Regeneration of Catalyst

Figure 5 shows the changes in the relative activity of the catalyst and the relative concentration of active sites during runs 21 to 27. Here, the relative activity and concentration were estimated by using equations (4) and (6) and on the basis of the initial activity of run 22, *i.e.*, the rate of reaction of fresh catalyst just treated with oxygen-saturated alkaline solution. The catalyst activity is assumed not to decline further during the oxygen treatment period (runs 21 and 24).

During the stopping period while the catalyst is being kept in the reaction mixture, the oxidized species are thought to be gradually reduced to I as the environment becomes oxygen-deficient, resulting in the increase in catalyst activity (as shown by the dotted line), though the total concentration of active species decreases probably due to the adsorption of some by-products and/or catalyst poisoning.

On the other hand, the treatment of deactivated catalyst with formalin solution results in a partial restoration of both the catalyst activity and the concentration of active sites. The increase in the number of active sites is ascribed to the reactivation of a fraction of the inactive species IV and/or desorption of the reaction products from the catalyst surface as the catalyst was repeatedly washed before and after the formalin treatment with distilled water. A new experiment was carried out under standard conditions: after a 4 h run, the catalyst

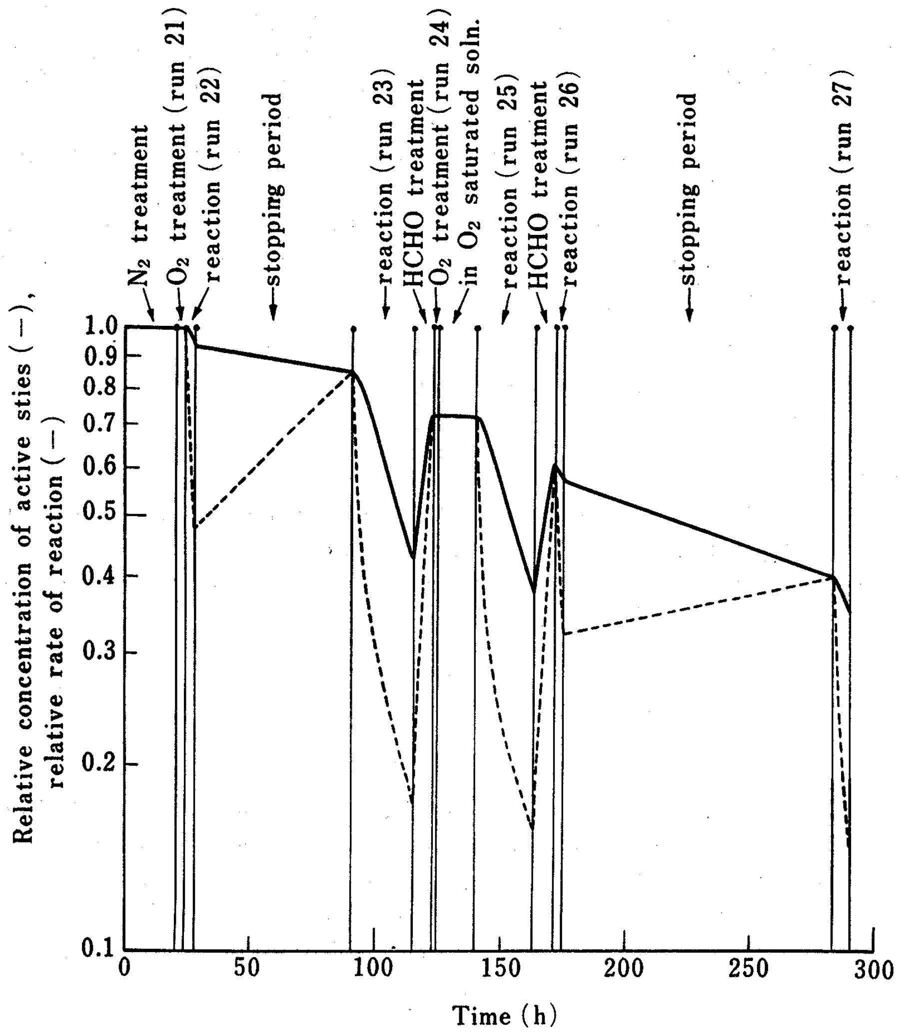

Fig. 5. Decay of Catalyst Activity and Regeneration of Catalyst

——, relative concentration of active sites; ······, relative rate of reaction.

(used) was thoroughly washed with warm distilled water (40°C, for 2 h). Then, after treatment of the catalyst (washed) with oxygen-saturated alkaline solution, the reaction was again started by feeding fresh reaction mixture (oxygen-saturated) into the reactor. The initial rate in this case was much higher than that at the end of the previous run, which indicated that the catalyst activity could be partly reversed by washing the catalyst with water. To check whether PtO_2 can be reduced to Pt or not, PtO_2/C catalyst was treated with formalin solution. The treated catalyst was found to exhibit no activity at all.

In Fig. 6, the global rates of reaction for runs 33 and 35 (before and after the reduction of the deactivated catalyst with hydrogen) are plotted as a function of time. The initial rate for run 35 (after reduction) is more than 40% higher than that for run 33 (before reduction). This indicates that a fraction of the deactivated (poisoned) sites which could not be reactivated by the formalin treatment are reactivated by hydrogen reduction. Since the deactivated catalyst was treated with oxygen gas for 4 h at 300°C before passing hydrogen gas through the reactor, the poison (supposed to be strongly adsorbed on the catalyst surface) might have been desorbed and/or oxidized, resulting in the increase in the number of active sites.

Conclusion

The oxidation of ethylene glycol on Pt/C catalyst was carried out in a liquid-full reactor, and the deactivation and regeneration of the catalyst were studied. The conclusions are as

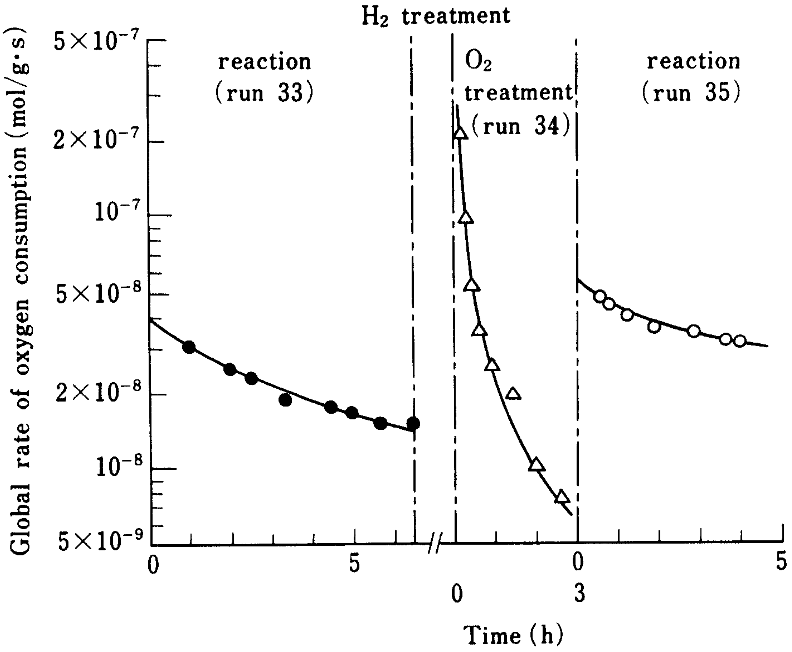

Fig. 6. Regeneration of Catalyst by Hydrogenation

Concentration of ethylene glycol (mol/cm^3), 0.1×10^{-3}; concentration of NaOH (mol/cm^3), 0.1×10^{-3}; amount of catalyst (g), 0.76; ●, run 33; △, run 34; ○, run 35.

follows.

(i) The fresh catalyst in a reduced state (Pt/C) exhibits a high activity and on oxygen treatment quickly adsorbs oxygen.

(ii) The adsorbed oxygen cannot be easily displaced by nitrogen.

(iii) The activity of the oxygen-treated catalyst during the course of an experiment declines rapidly over the initial period (~4 h) and then gradually as the reaction continues. This anomalous deactivation of the catalyst is attributed to the change in the composition of the oxidized (active) species involved in the reaction and to catalyst poisoning .

(iv) The catalyst deactivation can be reversed mainly by temporarily stopping the reaction and/or treating the catalyst (used) with formalin. The reactivation of catalyst during the stopping period is considered to be due to the reduction of oxidized platinum by ethylene glycol in the absence of oxygen.

(v) The regeneration of catalyst activity by formalin is ascribed to the reduction of oxidized platinum to platinum, as well as to the desorption of the poison due to washing with distilled water.

(vi) The extent of catalyst reactivation by hydrogenation is greater than that by formalin treatment or by stopping the reaction; this can be ascribed to the reduction of oxidized species by hydrogen and almost complete removal of the poison by washing and oxidation at high temperature before hydrogenation.

References and Notes

1) G.E. Brown, Jr. (Conen Co.), U.S. Patent 3879452 (1971).
2) T. Kiyoura (Mitsui Toatsu Chem. Co. Ltd.), Japan Kokai Patent 51-86413 (1976), 51-131824 (1976), 53-77009 (1978); M. Miya and T. Imamura (Kaoo Sekken Co. Ltd.), Japan Kokai Patent 52-116415 (1977), 52-128371 (1977).
3) J. Klassen and R.S. Kirk, *A.I. Ch. E. Journal*, **1**, 488 (1955).
4) M.I. Ali Khan, Y. Miwa, S. Morita, and J. Okada, *Chem. Pharm. Bull.*, **29**, 1795 (1981).

5) M.I. Ali Khan, Y. Miwa, S. Morita, and J. Okada, *Chem. Pharm. Bull.*, **29**, 1802 (1981).
6) J. Weber and G. Schnuchel (Erdoelchemie G.m.b.H.), Ger. Offen 2407146 (1975).
7) H. Saito (Kawaken Fine Chemical Co. Ltd.), Japan Kokai Patent 53-98923 (1978).
8) E.P. DiBella (Tenneco Chemicals Inc.) U.S. Patent 3673257 (1970); L.S. Bechara (Air Products and Chamicals, Inc. (U.S. Patent 3717676 (1971).
9) M.I. Ali Khan, Y. Miwa, S. Morita, and J. Okada, *Chem. Pharm. Bull.*, accepted.
10) J.M.H. Dirkx and H.S. Van der Baan, *J. Catalysis*, **67**, 1 (1981).
11) P.B. Weisz, *Z. Phys. Chem.*, **11**, 1 (1957).
12) O. Levenspiel, *J. Catalysis*, **25**, 265 (1972); J.M. Smith, "Chemical Engineering Kinetics," third edition, McGraw-Hill, Tokyo, 1981, p. 381.