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Liquid-phase Oxidation of Ethylene Glycol on a Pt/C Catalyst. II.[1] Kinetic Studies

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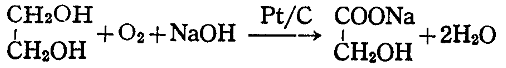
Catalytic oxidation of ethylene glycol in an alkaline aqueous solution over a Pt/C catalyst by oxygen was studied in a slurry reactor at 40°C and ambient pressure. Under our experimental conditions, the interphase and intraparticle mass transfer resistances were found to be insignificant. The catalyst deactivation observed during the course of experiments can be ascribed to the formation of some oxidized species of platinum and/or to the adsorption of some by-products on the catalyst surface, and the decay of catalyst activity is consistent with a first order consecutive process, as described in the previous paper.[1] The rate of reaction can be expressed by a power-law model under the conditions used. The orders of reaction with respect to ethylene glycol, sodium hydroxide and oxygen were estimated to be 0.20, 0.34 and zero, respectively. The mechanism of this reaction is discussed.

Keywords——ethylene glycol; liquid-phase; oxidation; platinum-on-carbon catalyst; deactivation; kinetics; slurry reactor

On platinum-group metal catalyst, alcohols and carbohydrates can be smoothly oxidized to the corresponding carboxylic acids by oxygen in basic aqueous solution. A number of papers and patents[2-6] are available on this reaction system. However, the data reported are mainly concerned with conversions obtainable under different process conditions and with different catalysts, and little information is available regarding the kinetics, reaction mechanism, or catalyst deactivation.

In a previous paper[4] on the liquid-phase oxidation of diethanolamine by oxygen over a Pd/Al_2O_3 catalyst, the rate-controlling step was found to be the oxidation of adsorbed diethanolamine. A similar conclusion was reached for the oxidation of ethanol on a Pd/Al_2O_3 catalyst by Ruether *et al.*[5] Recently, Dirkx *et al.*[6,7] investigated the kinetics of liquid-phase oxidation of glucose and gluconic acid on a Pt/C catalyst and found that strong inhibition of the catalyst activity took place during the course of an experiment. A mechanistic model was developed in which the interaction between oxygen and platinum catalyst was a very important factor.

In the previous work,[1] the liquid-phase oxidation of ethylene glycol over a Pt/C catalyst (eq. (1)) was investigated in a packed-bed flow reactor through which oxygen-saturated alkaline solution of ethylene glycol was passed continuously (hereafter referred to as a liquid-full reactor), and the deactivation and regeneration of the catalyst were discussed in detail.



$$\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}+O_2+NaOH\xrightarrow{Pt/C}\begin{matrix}COONa\\|\\CH_2OH\end{matrix}+2H_2O \qquad (1)$$

The deactivation of the catalyst was ascribed to the formation of some oxidized species of platinum as well as to the adsorption of some reaction by-products, and a consecutive deactivation model was proposed.

In the present work, investigations were undertaken on the kinetics and reaction mechanism of this reaction in a slurry reactor, and the adequacy of the previously proposed deactivation model[1] was examined.

Experimental

Unless otherwise stated, the same chemicals as described in the preceding paper[1] were used.

Catalyst Preparation——The catalyst was prepared by the same method as reported in the preceding paper.[1] An aqueous solution of required amount of hexachloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$) was added to a calculated quantity of 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. The adsorbed acid was reduced by slow addition of 37% formaldehyde solution (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 being washed with distilled water (till neutral), the catalyst was dried *in vacuo* at 80°C. Thereafter, the catalyst was crushed and sieved to obtain particles smaller than 250 mesh. The powdered catalyst was stored in a closed container under room conditions.

Apparatus and Procedure——Unless otherwise mentioned, all experiments were carried out in a stirred tank glass reactor (7.0 cm i.d. and 9.2 cm high) placed in a thermostated bath. Four evenly spaced vertical baffles (9.0 cm high and 7.0 cm wide) were fitted to the wall of the reactor. A six-bladed turbine (3.0 cm in diameter) was used for agitation. Oxygen gas or air was sparged into the liquid-phase continuously during the reaction, that is the gasphase was a flow system.

After charging of the reactor with an aqueous solution of sodium hydroxide, an appropriate quantity of the powdered catalyst was added. In order to treat the catalyst completely with oxygen, oxygen gas was continuously bubbled through the reactor for 1 h at 40°C. Then, the reaction was started by adding ethylene glycol, and samples were taken at intervals of 10—20 min. Unless otherwise stated, the reaction conditions mentioned in Table I were used.

TABLE I. Experimental Conditions

Reaction temperature, °C	40.0
Total metal content of catalyst, wt%	0.2
Catalyst particle size, mesh	−250
Catalyst loading, g/cm^3	0.5—1.0×10^{-2}
Concentration of ethylene glycol, mol/cm^3	0.5—3.0×10^{-4}
Concentration of sodium hydroxide, mol/cm^3	0.5—3.0×10^{-4}
Concentration of oxygen, mol/cm^3	0.19—0.96×10^{-6}
Gas flow rate, cm^3/s	0.57
Stirring speed, rpm	1800
Total pressure, atm	1.0

Analysis——The glycolic acid produced was isolated as its *p*-bromophenacylester[8] (mp 137—138°C), which was identified by comparing its infrared (IR) spectrum with that of an authentic sample. Under our experimental conditions oxalic acid was not detected.

The yield of glycolic acid was determined titrimetrically. The conversion of ethylene glycol was measured on a gas chromatograph with a 2 m glass column (3 mm i.d.) packed with 100—200 mesh particles of Porapak Q. The column temperature was maintained at 120°C. Results obtained by both methods agreed to within ±5%. Thus, the rate of reaction of ethylene glycol was considered to be equal to the rate of formation of glycolic acid. The rate data given hereafter were calculated from the titrated amount of glycolic acid.

Results and Discussion

The deactivation model proposed in the preceding paper[1] is illustrated in Chart 1. The fresh catalyst in the reduced state (referred as Catalyst I) was found to exhibit a very high

$$\begin{array}{cccc} \text{Catalyst I} & \xrightarrow{\text{oxygen treatment}} & \text{Catalyst II} & \xrightarrow[k_2]{\text{reaction}} \\ \text{(Pt)} & & (\text{Pt O}_2) & \\ \text{very high activity} & & \text{high activity} & \end{array}$$

$$\begin{array}{ccc} \text{Catalyst III} & \xrightarrow[k_3]{\qquad\qquad} & \text{IV} \\ \text{(some oxidized species)} & & \text{(unknown)} \\ \text{mild activity} & & \text{no activity} \end{array}$$

Chart 1

activity, but on oxygen treatment was deactivated to Catalyst II due to adsorption of oxygen on the catalyst surface. In the course of reaction, the catalyst activity declined rapidly over an initial period of five hours and then declined gradually as the reaction continued. The deactivation was ascribed to both formation of some oxidized species of platinum and catalyst poisoning due to irreversible adsorption of reaction by-products. Since the catalyst used in the present study, after preparation, was stored under room conditions, a fraction of the active sites had probably adsorbed atmospheric oxygen, and the true initial rate of reaction on Catalyst I thus could not be measured. For this reason, experiments were carried out with oxygen-treated catalyst (Catalyst II) and the observed rate of reaction is considered to be the rate of reaction on Catalyst II.

The data plotted in Fig. 1 show the dependence of the initial rate of reaction, r_{A0} (mol/cm^3·s), upon the catalyst loading, m (g/cm^3) and the stirring speed (rpm). C_A, C_B and C_N (mol/cm^3) stand for the concentrations of ethylene glycol, oxygen and sodium hydroxide, respectively. There is a linear relationship between r_{A0} and m, and the rate is independent of the stirring speed above 1800 rpm. These results suggest that under our experimental conditions at a stirring speed of 1800 rpm or above, the interphase (gas-to-liquid and liquid-to-solid) mass transfer resistances can be neglected. Calculations based on the available correlations[9] also indicate that under the present conditions all mass transfer resistances (interphase and intraparticle) are insignificant. Based on the observations presented above, kinetic control can be assumed at 1800 rpm or above. A modelling of the reaction in the kinetic regime was, therefore, attempted.

The dependence of the initial rate of reaction on ethylene glycol, oxygen and sodium hydroxide concentrations is illustrated in Figs. 2 and 3. The estimated orders of reaction are compared with those obtained in the liquid-full reactor in Table II. In the case of the liquid-full reactor, the reaction was carried out under the same conditions as applied in the preceding paper[1] and was continued for 40 h. Then, the rate of reaction was measured while the concentration of each component was changed. It can be assumed that during 40 h operation, Catalyst II is totally deactivated to Catalyst III and to some inactive species IV as described previously.[1] Therefore, the obtained orders in the liquid-full reactor are considered to be the reaction orders for Catalyst III.

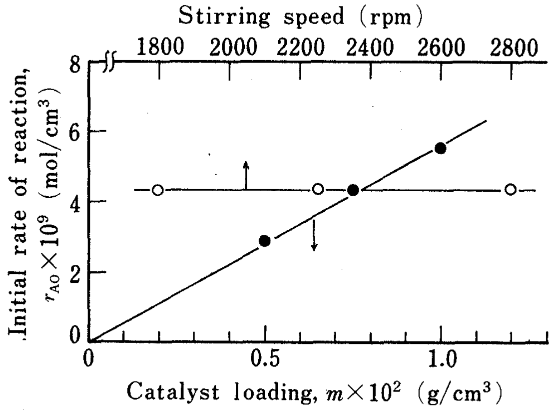


Fig. 1. Dependence of Initial Rate of Reaction on Catalyst Loading, m (g/cm^3) and Stirring Speed (rpm)

Reaction temperature 40°C, $C_A=1.0\times10^{-4}$ mol/cm^3, $C_B=0.96\times10^{-6}$mol/cm^3, $C_N=1.0\times10^{-4}$ mol/cm^3.

The fractional orders obtained in both cases differ only slightly from each other. This indicates that the reactions taking place on Catalyst II (in the case of slurry reactor) and Catalyst III (in the case of liquid-full reactor) may follow more or less similar mechanisms.

To study the influence of the concentration of reaction product (glycolic acid) on the rate of reaction, an experiment was carried out by adding sodium glycolate (30% molar amount with respect to ethylene glycol) to the initial reaction mixture. The observed rate of reaction seemed not to be affected by the addition of sodium glycolate. Therefore, it is concluded that the catalyst poisoning, which was ascribed to the adsorption of reaction products,[1] is not due to the adsorption of glycolic acid, but might be due to adsorption of some by-products.

The conversion profiles for different catalyst loadings, the initial molar ratios of sodium hydroxide to ethylene glycol and the concentrations of oxygen are shown in Fig. 4. The data represented by open (—○—) and solid (—●—) circles suggest the independence of the rate of reaction upon oxygen concentration.

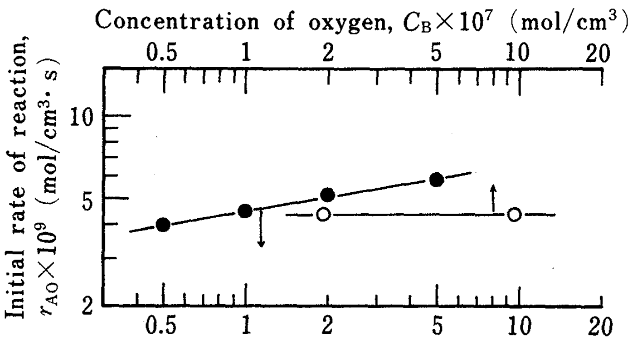


Fig. 2. Effects of Concentrations of Ethylene Glycol and Dissolved Oxygen on the Initial Rate of Reaction

$C_N = 1.0 \times 10^{-4}$ mol/cm³, $m = 0.75 \times 10^{-2}$ g/cm³.

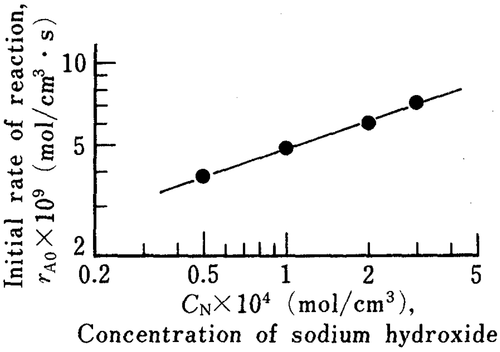


Fig. 3. Effect of Concentration of Sodium Hydroxide on the Initial Rate of Reaction

$C_A = 1.0 \times 10^{-4}$ mol/cm³, $C_B = 0.96 \times 10^{-6}$ mol/cm³, $m = 0.75 \times 10^{-2}$ g/cm³.

TABLE II. Comparison of Rate Orders

Reactant	Slurry reactor[a]	Liquid-full reactor[b]
Ethylene glycol	0.20	0.39
Sodium hydroxide	0.34	0.22
Oxygen	0.00	0.00

a) Rate orders for the reaction on Catalyst II.
b) Rate orders for the reaction on Catalyst III.

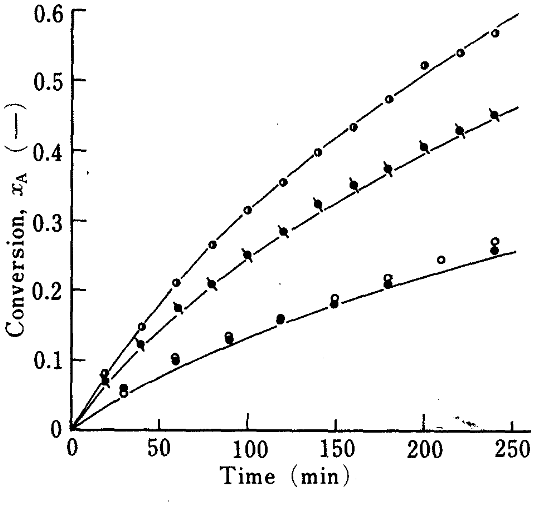


Fig. 4. Ethylene Glycol Conversion Profiles

$C_A = 1.0 \times 10^{-4}$ mol/cm³.

Symbols (oxygen concentration C_B (mol/cm³), initial molar ratio of sodium hydroxide to ethylene glycol n, catalyst loading m (g/cm³)): ◑, 0.96×10^{-6}, 2.0, 1.5×10^{-2}; ●, 0.96×10^{-6}, 1.0, 1.5×10^{-2}; ○, 0.96×10^{-6}, 1.0, 0.75×10^{-2}; ●, 0.19×10^{-6}, 1.0, 0.75×10^{-2}.

In accordance with the previously proposed deactivation model (Chart 1), the catalyst deactivation in the present case is assumed to proceed by the following consecutive first order process.

$$\text{Catalyst II} \xrightarrow{k_2} \text{Catalyst III} \xrightarrow{k_3} \text{IV} \qquad (2)$$

Here, k_2 and k_3 are the respective rate constants. Assuming the activity of the catalyst at the start of the reaction to be unity, the activity at time t (θ_t) can be expressed as

$$\theta_t = K \exp(-k_2 t) + (1-K) \exp(-k_3 t) \qquad (3)$$

$$\text{where} \quad K = 1 - \frac{k_2}{k_2 - k_3}\alpha \qquad (4)$$

Here, α(—) is the relative activity of Catalyst III with respect to Catalyst II ($\alpha < 1$).

As described earlier (Table II), the difference between the orders of reactions obtained in the slurry reactor (Catalyst II) and in the liquid-full reactor (Catalyst III) is small, and since in the present case the reaction was continued for not more than 5 h, the contribution of reaction on Catalyst III to the overall reaction can be considered small. Thus, the orders of reaction for Catalyst III are assumed to be the same as those for Catalyst II. Therefore, the rate of reaction at time t can be expressed as

$$\begin{aligned} -\frac{dc_A}{dt} &= k_0 \cdot m \cdot \theta_t \cdot c_A \cdot^{0.20} \cdot c_N^{0.34} \\ &= k_0 \cdot m \, \{k \exp(-k_2 t) + (1-k) \exp(-k_3 t)\} \, c_A^{0.20} \cdot c_N^{0.34} \end{aligned} \tag{5}$$

where k_0 is the reaction rate constant obtained from the initial rate of reaction. As the reaction is equimolar in ethylene glycol and sodium hydroxide, the rate of reaction can be rewritten as

$$\frac{dx_A}{dt} = \frac{k_0 m}{c_{A_0}{}^{0.46}} \{k \exp(-k_2 t) + (1-K) \exp(-k_3 t)\} x_A^{0.20} \cdot (n - x_A)^{0.34} \tag{6}$$

where x_A is the conversion of ethylene glycol, n is the initial molar ratio of sodium hydroxide to ethylene glycol, and C_{A_0} is the initial concentration of ethylene glycol. Now k_0 can be evaluated from the initial rate of reaction, and the values of K, k_2 and k_3 were estimated in the previous work.[1] These values are summarized in Table III. The curves calculated by the numerical integration of eq. (6) with these values are shown in Fig. 4. These curves are in good agreement with our experimental results. Thus, the deactivation model proposed previously[1] is also applicable to the results obtained in the slurry reactor.

TABLE III. Parameter Values

k (—)	$0.51^{a)}$
k_2 (s^{-1})	$2.1 \times 10^{-4\,a)}$
k_3 (s^{-1})	$8.3 \times 10^{-6\,a)}$
k_0 ($mol^{0.46} \cdot cm^{1.62} \cdot g^{-1} \cdot s^{-1}$)	$5.6 \times 10^{-5\,b)}$

a) Estimated in the previous work.[1]
b) Estimated from the initial rate of reaction.

As reported in the preceding paper,[1] the reduced catalyst (Catalyst I) was found to exhibit a very high activity but on treatment with oxygen was deactivated to Catalyst II. The rate of reaction is independent of the concentration of oxygen, as suggested by the experimental data in Figs. 1 and 4. Therefore it is considered that the adsorption of oxygen on Catalyst I is fast and almost irreversible, and that all the active sites are covered with adsorbed oxygen.

Analogous phenomena were found by Dirkx *et al.*[7] in the liquid-phase oxidation of gluconic acid over a Pt/C catalyst. A much higher initial rate of reaction was obtained with reduced catalyst than when the catalyst was initially contacted with oxygen. However, the rate of reaction was found to decrease with increasing oxygen concentration. The decline of catalyst activity was ascribed to the decrease of reduced sites due to the chemisorption of oxygen. Gluconic acid was assumed to be adsorbed on the residual reduced platinum sites and was oxidized to L-glucaric acid *via* the formation of guluronic acid by adsorbed oxygen. The adsorption of oxygen on the catalyst surface was considered to be fast and reversible.

The observed fractional order (0.20) with respect to ethylene glycol also suggests its adsorption on the catalyst surface. However, in our case, the adsorption of ethylene glycol is considered to take place on Catalyst II, rather than on reduced platinum sites as proposed by Dirkx *et al.*[7] The reaction proceeds *via* the dehydrogenation of adsorbed ethylene glycol followed by oxidaton to glycolic acid.

In conclusion, the reaction scheme for the oxidation of ethylene glycol with Pt/C as a catalyst can be written as follows,

$$\mathrm{Pt} + \mathrm{O_2} \xrightarrow{\text{very fast}} \text{Catalyst II} \tag{7}$$

$$\mathrm{HOCH_2CH_2OH} + \text{Catalyst II} \rightleftharpoons (\mathrm{HOCH_2CH_2OH})_{ad} \tag{8}$$

$$(\mathrm{HOCH_2CH_2OH})_{ad} \longrightarrow \mathrm{HOCH_2CHO} + (\text{Catalyst II} - \mathrm{H_2}) \tag{9}$$

$$HOCH_2CHO \longrightarrow HOCH_2COOH \qquad (10)$$

$$(\text{Catalyst II}-H_2) + 1/2\,O_2 \longrightarrow \text{Catalyst II} + H_2O \qquad (11)$$

where ($)_{ad}$ indicates an adsorbed species.

In this reaction scheme, the dependence of the rate of reaction on the concentration of sodium hydroxide is not taken into account. Since sodium hydroxide promotes the oxidation of ethylene glycol (Fig. 3), a detailed study regarding its role is necessary for a clear understanding of the reaction mechanism.

References and Notes

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