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# Palladium on alumina catalyst for glucose oxidation: reaction kinetics and catalyst deactivation

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**Abstract**

The paper presents a study on glucose oxidation over a modified palladium/alumina catalyst in a weak alkaline medium. The high reaction rates and complete conversion obtained are explained by non-uniform distribution of the active metal within the catalyst support and also by the raised number of Pd atoms on the active particles surface. Catalyst deactivation is described as a process caused by Pd–O formation in the metal lattice accompanied by adsorption of the reaction products. The effects of catalyst mass, particle diameter, multiple use of the catalyst and initial glucose concentration on the conversion were investigated. The kinetic constants are determined using the single site Langmuir–Hinshelwood model.

## 1. Introduction

Selective glucose oxidation to gluconic acid and glucoronic acid is becoming very important in the food and pharmaceutical industries. A possible new application is the use of the oxidation product as a substitute for polyphosphates in detergents. Therefore, glucose oxidation has been subject to numerous investigations [1–4]. They concern mainly two basic methods: three-phase catalytic oxidation and biocatalytic oxidation. With regard to catalytic oxidation, several problems have been considered: catalyst type, reaction rate and catalyst deactivation.

The use of platinum on active carbon as a catalyst causes fast initial glucose reaction with oxygen to gluconic acid in a weakly alkaline medium [4]. Side reactions are also found to take place and form uronic acids. During the experiments, the Pt/C catalyst is highly deactivated. However, it is partially recovered by temporary replacement of the oxygen flow by a nitrogen flow. The catalyst deactivation is explained by the formation of platinum oxide (PtO). The fall in reaction rate is ascribed to the following factors:

- a gradual decrease of glucose concentration;
- adsorption of the reaction products on the catalyst;
- catalyst deactivation;
- the change in pH of the reaction mixture.

In parallel to the above investigations (in a suspended bed), the same catalyst (Pt/C) has been tested in a fixed-bed reactor [5]. Two principle results were obtained:

(1) in the range of experimental conditions studied, liquid–solid contacting efficiency was nearly constant;

(2) no significant change of reaction rate with superficial gas (oxygen) velocity was registered.

The most important problem during glucose oxidation is the deactivation of platinum catalysts [4,6]. The problems of the catalyst deactivation

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and its price led to the development of new catalysts on the base of palladium: Pd/C, Pd–Bi/C, Pd–Pt–Bi/C [1,2]. The palladium catalysts (Pd/C) used in glucose oxidation are also poisoned by oxygen and this poisoning is particle-size dependent. However, it was shown that a relatively rapid and total conversion of glucose can be achieved by adding promoters like bismuth [1].

The data available in the literature show that the catalysts used in glucose oxidation usually contain 5% Pt or Pd uniformly deposited on carbon supports [1,2,4–6].

With the further aim of ensuring easy removal of the catalyst from the reaction mixture and to enhance its mechanical stability, as well as to enable operation in a fixed or/and suspended bed, the present work was concentrated on glucose oxidation kinetics over a modified Pd catalyst on alumina supports.

## 2. Experimental

### 2.1. Experimental set up

The experiments were carried out in a reactor (Trinquart–Toulouse) illustrated in Fig. 1. The reactor consists of two parts: a removable cap with four holes and a vessel. The value of pH was measured and controlled by an automatic titrator (Radelkis). The temperature was maintained within the range 50–60°C by using a thermostat (MLW). A propeller stirrer (Janke and Kunkel) was used for mixing the slurry.

### 2.2. Phase description

#### 2.2.1. Solid phase

As solid phase, a catalyst consisting of 0.5% Pd on alumina tablets was used. The catalyst was ground to a fraction below 0.045 mm and another fraction between 0.045 and 0.08 mm. The Pd content was determined by using a scanning electronic microscope (Philips). Usually, the experiments were performed at a catalyst concentration of 35 g/l at an active metal concentration of 0.175 g/l.

#### 2.2.2. Liquid phase

Anhydrous D-(+)-glucose was used as the reactant (Janssen). The glucose concentration was varied from 0.4 to 1.6 mol/l and was determined by using a HPLC (Perkin and Elmer). The pH of the slurry was kept constant by titration with sodium hydroxide solution.

#### 2.2.3. Gas phase

Glucose oxidation was carried out in a weak alkaline aqueous medium (NaOH) with air as oxidizing agent at a predominant temperature of

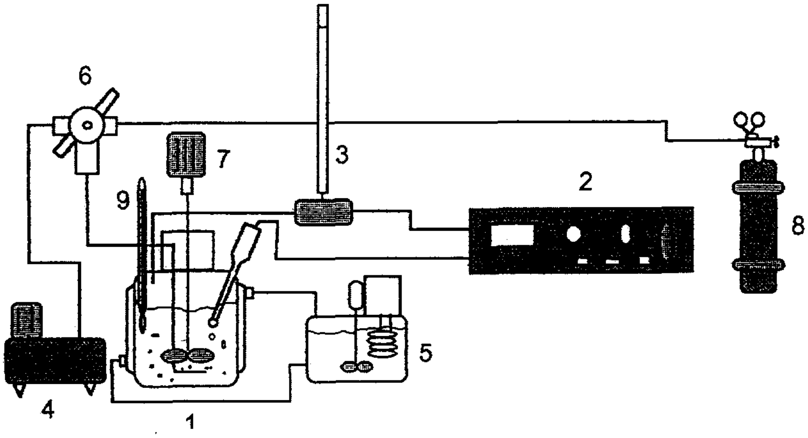

Fig. 1. Experimental set up. (1) Kinetic reactor, (2) automatic titrator, (3) automatic burette, (4) air pump, (5) thermostat, (6) three-way valve, (7) stirrer, (8) nitrogen, (9) thermometer.

50°C and atmospheric pressure. The concentration of oxygen in the slurry was measured with an oxygen probe (Ingold sterilizable electrode) which displays the equivalent saturation pressure of the oxygen dissolved in the slurry. While it was impossible to determine the influence of the temperature on all the rate and adsorption constants, maintaining the temperature at 50°C enabled us to avoid temperature dependence on reaction rates and adsorption equilibria.

### 2.2.4. *Start-up procedure*

The catalyst suspension was brought to the required temperature in a nitrogen atmosphere. After introducing the concentrated glucose solution into the reactor, nitrogen was fed into the reactor for an additional 15 min. Thereafter, the nitrogen flow was stopped and the experiment was started by introducing air. Samples for analysis were taken during the whole process.

Following the end of the process, the catalyst was filtered off and washed with hot DI water until the filtrate become neutral. The catalyst was dried at 50°C and sieved to remove fines.

## 3. Results and discussion

A review of the literature shows that during the process the rates of glucose oxidation go down with glucose consumption. Several causes have been considered for the explanation of this phenomenon: catalyst type and particle diameter, glucose concentration, adsorption of reaction products and catalyst deactivation. Since a decrease of the reaction rate is not always confirmed in the literature, in the present study special attention has been paid to this subject.

The influence of particle diameter on glucose conversion is shown in Fig. 2.

In both experiments, 1 and 2, the reaction rates were relatively identical. Particle sizes between 0.045 mm and 0.08 mm did not influence the process considerably.

Further, glucose conversion at different concentrations of the modified catalyst, was investigated (Fig. 3).

A concentration of 5% is high for a slurry reactor. Therefore, we choose a catalyst concentration of 3.5% with active metal 0.175 g/l. In this case, we obtained full glucose conversion (0.4 M) within 2 hours. Considering the price of precious metals, their amount in the catalyst pellets is an important factor. It is interesting to compare these results with the results of a series of experiments at the same conditions using an uniformly deposited catalyst [1,4]. These authors used a concentration of active metal in the range 0.2–0.4 g/l. The comparison is illustrated in Fig. 4.

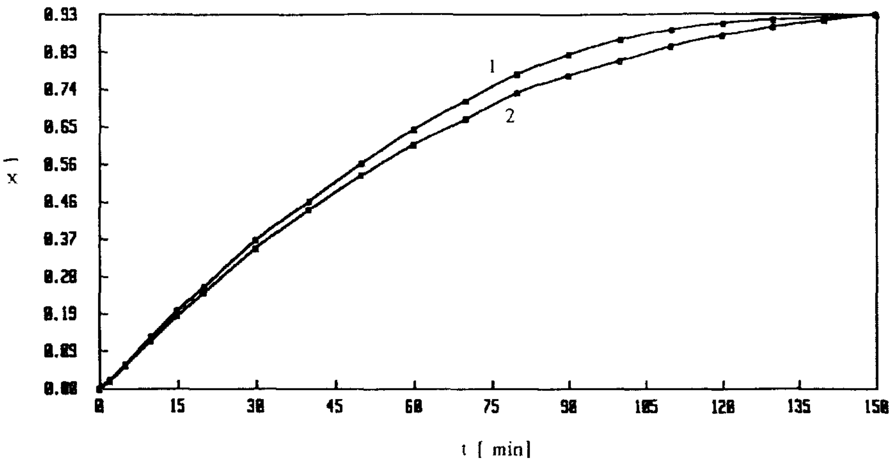

Fig. 2. The effect of particle diameter on glucose conversion: (1) fraction below 0.045 mm, (2) fraction between 0.045 and 0.08 mm. [G] = 0.4 mol/l in 2.5% catalyst suspension.

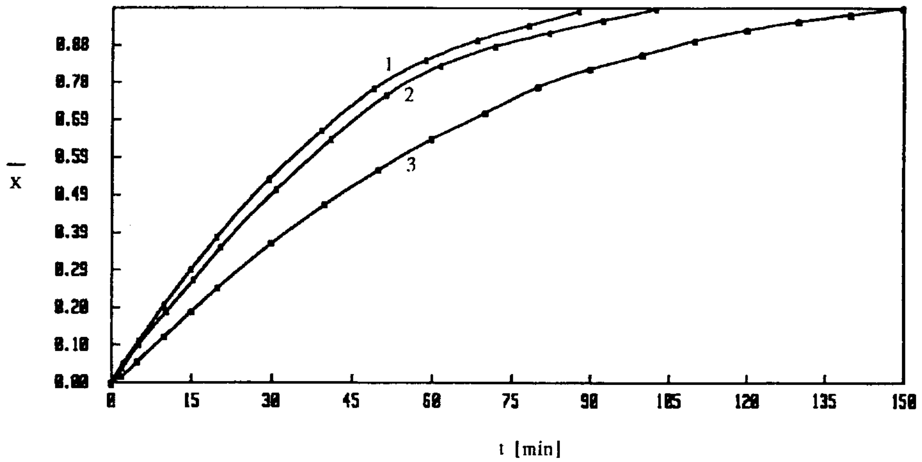

Fig. 3. Glucose conversion as a function of the amount of catalyst (1) 5%; (2) 3.5%; (3) 2.5%.

The higher activity of the modified Pd/AlO$_3$ catalyst is obvious. The experiments carried out with a non-coated AlO$_3$ does not show any catalyst activity within a time range of 30 min.

In the experiments described, a part of the change of the reaction rate may be caused by the decrease of glucose concentration (curves 1 and 4, Fig. 4). Although this effect is not large, as shown in Fig. 5, we undertook a number of experiments in which [G] was kept constant (within 5%) by adding concentrated glucose solution commensurate with caustic soda consumption. As the order of the reaction rate in glucose is small, small variations of [G] would affect the reaction rate only negligibly.

The reaction rate, at standard conditions ([G] = 0.4 mol/l at 0.175 g/l active metal, $T$ = 50°C, pH = 9) is plotted as a function of reaction time in Fig. 6.

It can be seen that the reaction rate decreases vigorously with time. At standard conditions, the decrease of the reaction rate could be caused by

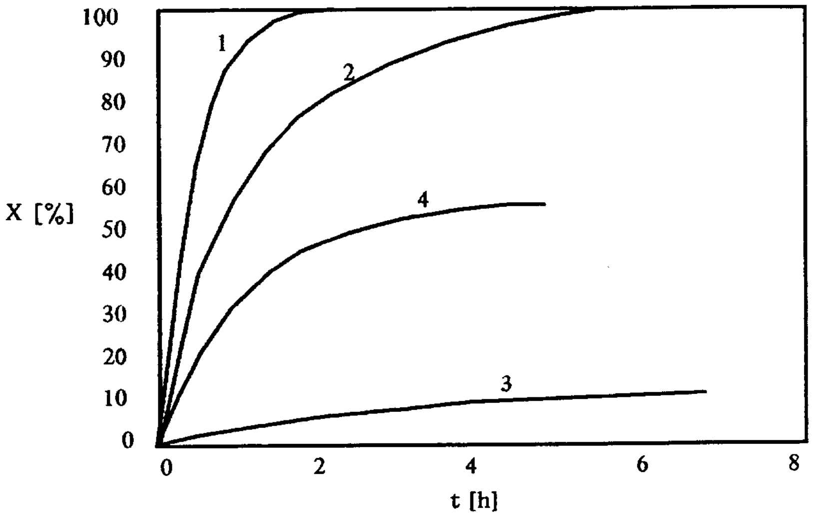

Fig. 4. Comparison of the performance of the catalyst reported by various authors. (1) Pd/Al$_2$O$_3$ (0.5 wt.-% Pd). [G] = 0.4 mol/l at 0.175 g/l active metal; $T$ = 55°C and pH = 9 — this work. (2) Pd–Bi/C (5 wt.-% Pd and 2 wt.-% Bi), experimental conditions are not specified [1]. (3) Pd/C (5 wt.-% Pd) — experimental conditions are not specified [1]. (4) Pt/C (5 wt.-% Pt). [G] = 0.2 mol/l on 0.2 g/l active metal; $T$ = 55° and pH = 9 [4].

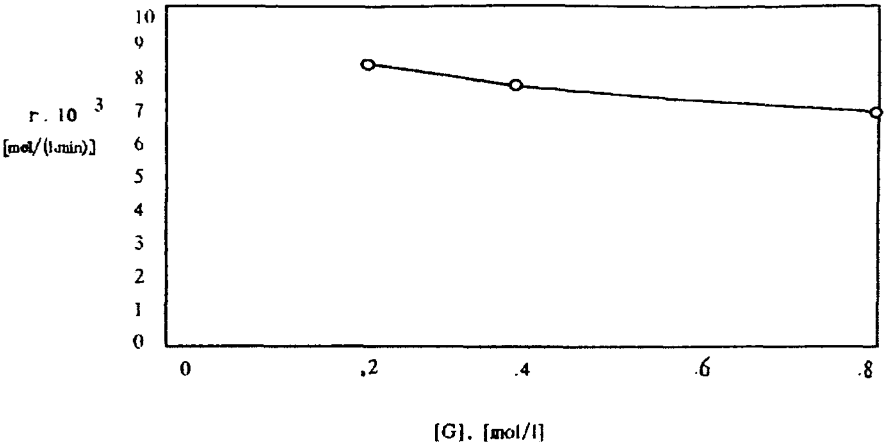

Fig. 5. Rate dependence with respect to initial glucose concentration.

adsorption of reaction products on the catalyst surface or/and catalyst deactivation during the experiment. Preliminary experiments showed that some of the decrease of the reaction rate is caused by adsorption of reaction products on the catalyst surface. These experiments helped to compare the conversion obtained in the case of fresh catalyst + fresh glucose solution (experiment 1) with the rate in the case of fresh catalyst + reaction mixture from the previous experiment (experiment 2). In both cases the glucose concentration was the same. Experiment 2 showed lower conversion than experiment 1. Similar results have been obtained by Dirkx and van der Baan [4] for the Pt/C catalyst. During the experiment, part of the initial reaction rate could be recovered by interruption of the oxygen supply to the reactor (Fig. 7).

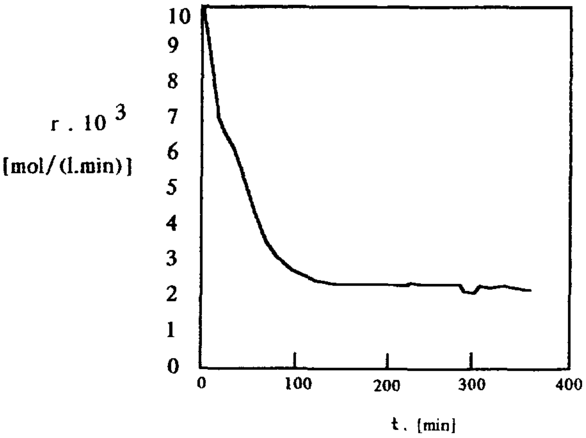

Fig. 6. Time-course of reaction rate.

From these results and also from the data available in the literature [4,6] it can be concluded that the most important factor which affects the rate of deactivation is oxygen concentration in the liquid. Accordingly, catalyst deactivation can be principally ascribed to the presence and action of oxygen. Two mechanisms are considered:

(1) catalyst deactivation is ascribed to the formation of metal oxide (PtO) [4];

(2) a diffusion model is suggested based on oxygen penetration in the upper layers of metal (platinum or palladium) lattice [6].

The diffusion model proposed agrees with the high activity of the modified Pd/AlO$_3$ catalyst used in this work. In fact, the catalyst consists of particles of two types: particles with catalytic material distributed non-uniformly in the support and particles which are uniformly distributed. It should be noted that following the grinding the ratio of the number of Pd atoms on the surface of the active particle to their number in the particle volume is raised.

According to the diffusion model of Dijkgraaf et al. [6], these catalytic characteristics can accelerate oxygen desorption from the palladium lattice and also, in general, the desorption of reaction products. Thus, the modified Pd/Al$_2$O$_3$ catalyst offers a higher reaction rate in comparison with

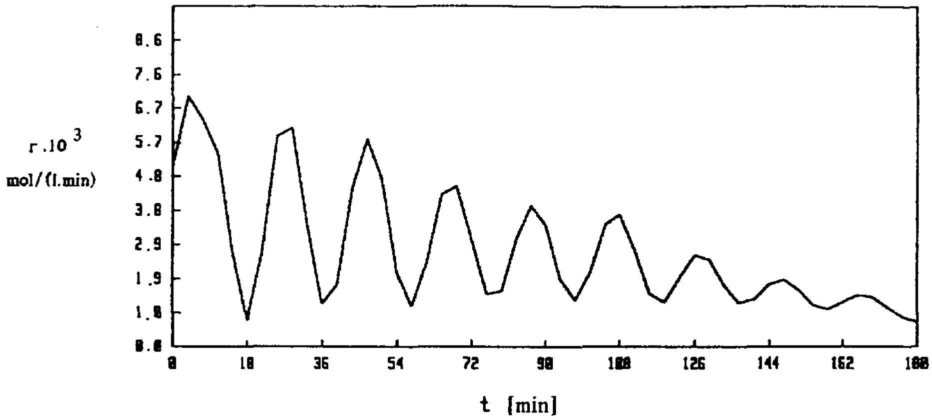

Fig. 7. Reaction rate obtained by 10 min gas flow-rate interruption intervals.

the other catalysts based on the uniform distribution of the Pd or Pt in the carbon support.

The effects of deliberate non-uniform distribution of the catalytic material within the support on the catalyst performance have been clarified by Gavrilidis and Varma [7]. These, as well as later studies, demonstrated that non-uniformly distributed catalysts can offer superior conversion, selectivity and durability over those distributed uniformly.

## 4. Kinetic study

On the basis of our results two possible cases or two mechanisms were considered, as follows:

(1) A case where the deactivation effect of the oxygen is eliminated. This situation is observed in the case of cyclic supply of gas. At the end of the regeneration period, it is assumed that the dissolved oxygen reacts directly with glucose molecules. In this case, as a first approximation, the reaction rate can be described by a single site Langmuir–Hinshelwood model:

$$\rightarrow r = -\frac{d[G]}{dt} = \frac{k[G]}{1+K[G]+K_p\Delta G}\cdot Mc \qquad (1)$$

It is assumed that product distribution remains constant during the experiment. The values obtained for the constants by a multiparametric optimization procedure and their values were: reaction rate constant, $k=0.0473$ [1/(g·min)]; adsorption constant for glucose, $K=0.0138$ [1/mmol]; adsorption constant for products, $K_p=0.0279$ [1/mmol]; $Mc$ is catalyst concentration [g/l].

For the same oxidation reaction on Pt/C catalyst, Dirkx and van der Baan [4], obtained the following values: $k=0.015$; $K=0.013$ and $K_p=0.021$.

(2) The second case considering oxygen dissolved in the Pd lattice, leads to a model with an oxidation–reduction reaction mechanism [8]. Since the initial glucose concentration does not affect the oxidation rate considerably, this model will be the subject of future investigations.

## 5. Nomenclature

| | |
|---|---|
| $[G]_0$ | Initial glucose concentration [mmol/l] |
| $[G]$ | Glucose concentration [mmol/l] |
| $r$ | Reaction rate [mmol/(l·min)] |
| $k$ | Reaction rate constant [l/(g·min)] |
| $K$ | Adsorption constant for glucose [l/mmol] |
| $K_p$ | Adsorption constant for products [l/mmol] |
| $t$ | Time [min] |
| $T$ | Temperature [°C] |
| $\Delta G$ | Change of glucose concentration [mmol/l] |
| $Mc$ | Catalyst concentration [g/l] |

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