JOURNAL OF CATALYSIS **150**, 199–211 (1994)

Direct Oxidation of L-Sorbose to 2-Keto-L-gulonic Acid with Molecular Oxygen on Platinum- and Palladium-Based Catalysts

C. Brönnimann,* Z. Bodnar,* P. Hug,† T. Mallat,* and A. Baiker*,[1]

*Department of Chemical Engineering and Industrial Chemistry, Swiss Federal Institute of Technology, ETH-Zentrum, Zürich CH-8092, Switzerland; and †Institute for Inorganic Chemistry, University of Zürich, Winterthurerstrasse 190, Zürich CH-8057 Switzerland

Received February 4, 1994; revised May 16, 1994

The selective oxidation of the C1 hydroxyl group of L-sorbose to a carboxylic group without protection of the four other hydroxyl functions was investigated. The reactions were performed in slightly alkaline aqueous solutions with molecular oxygen over various alumina- and carbon-supported Pt and Pd catalysts. Optimum reaction conditions were 50°C, pH 7.3, and a catalyst : reactant ratio of 1 : 4 (wt/wt). The lower the pH and the temperature, the higher the selectivity toward 2-keto-L-gulonic acid. Catalyst deactivation was also found to increase with lower pH and temperature. A 5 wt% Pt/alumina catalyst showed the best catalytic performance (67% selectivity at 58% conversion). Promotion with Bi or Pb had a detrimental effect on selectivity for 2-keto-L-gulonic acid. Electrochemical measurements indicated that the reaction occurs in a rather narrow potential range, which corresponds to a moderate oxygen coverage of Pt or Pd. Four types of catalyst deactivation processes were identified, based on XPS and ICP-AES analysis and on the *in situ* determination of the oxidation state by monitoring the catalyst potential during reaction. A significant chemical poisoning of the active noble metal sites occurred during the initial, destructive adsorption of L-sorbose and during the oxidation reaction. The successive contamination of active sites resulted in overoxidation (too high oxygen coverage of Pt or Pd). The partially oxidized promoters and noble metals were corroded and dissolved in the presence of 2-keto-L-gulonic acid, resulting in an irreversible deactivation.

INTRODUCTION

The heterogeneous catalytic oxidation of alcohols in aqueous solution with molecular oxygen is usually performed with supported Pt and Pd catalysts (1, 2). The oxidation of primary alcohols to aldehydes or carboxylic acids and of secondary alcohols to ketones is of great practical importance. Its mild reaction conditions and high selectivities (>90%) made the process important for the transformation of carbohydrates (3–5). The reactions are usually performed in a neutral or slightly alkaline medium under atmospheric pressure and at temperatures below 60°C in order to minimize the various side and consecutive reactions. The oxidation of D-glucose to D-gluconic or D-glucaric acid is one of the most investigated reactions in this field (6–11). The use of Pt/C or Pd/C catalysts results in 50–90% yields, with the formation of C1–C5 mono- and dicarboxylic acids as typical by-products (8, 12).

Modification of Pt and Pd catalysts with Bi, Pb, and several other metals has been suggested in order to suppress catalyst deactivation and improve selectivity (13–15). A trimetallic Pd–Pt–Bi/C catalyst was found to possess good activity in the oxidation of D-glucose with a selectivity higher than 96% for D-gluconic acid even at high conversion (16). An outstanding change from C6 to C2 oxidation selectivity was observed in the oxidation of D-gluconic acid by modification of a Pt/C catalyst with $Pb_3(PO_4)_2$ (13, 15). The higher selectivity toward 2-keto-D-gluconic acid was explained by Pb^{2+} complexation with the reactant. A similar change in selectivity was found in the electrochemical oxidation of D-gluconic acid on a polycrystalline Pt electrode modified by Pb adatoms (17).

In situ Bi^{3+} promotion of a Pd/C catalyst results in 100% selectivity to sodium lactobionate from lactose with conversions up to 95% (18). The penetration of Bi into the Pd crystal lattice and the formation of disperse Pd (14) or a geometric blocking of Pt active sites by Bi adatoms controlling the orientation of the reactant (19) were put forward to explain the role of Bi promotion.

It is generally accepted that the reaction mechanism is an oxidative dehydrogenation (4). According to this concept only the metallic sites are active (20, 22), which explains the necessary prereduction of the catalyst by hydrogen or by the reactant itself under a nitrogen atmosphere. It was proposed recently (21) that catalyst prereduction may be omitted in the joint oxidation of alcohol pairs, if one of the alcohols is a good reducing agent.

There exist contradictory explanations concerning the nature of catalyst deactivation. The first interpretation, which pointed to direct correlation between the transformation of metallic active sites to inactive oxides (usually termed "overoxidation") and the loss of activity, was

---

[1] To whom correspondence should be addressed.

0021-9517/94 $6.00

reported in the eighties (6, 23). Note that the oxidation state of the catalyst during reaction was not measured. It has been proposed recently (24–26) that catalyst overoxidation is not the cause but the result of deactivation. The primary reason is the initial destructive adsorption of the alcohol reactant on Pt or Pd, which results in the formation and irreversible adsorption of by-products. The phenomenon, termed "self-poisoning" in the electrocatalytic literature (27–30), has been widely investigated by electrochemical, *in situ* spectroscopic, and radiotracer methods in connection with the oxidation of alcohols and carbohydrates (27, 31, 32).

The aqueous phase oxidation of L-sorbose to 2-keto-L-gulonic acid (2-KLG) has been the subject of several investigations (39–41). Both compounds are intermediates in the production of L-ascorbic acid. The traditional path of this transformation includes three chemical steps, based on the Reichstein–Gruessner synthesis (33):

(i) Protection of L-sorbose by acetone, yielding 2,3 : 4,6-di-*o*-isopropylidene-α-L-sorbose.

(ii) Oxidation of 2,3 : 4,6-di-*o*-isopropylidene-α-L-sorbose to 2,3 : 4,6-diisopropylidene-2-keto-L-gulonic acid by aqueous NaOCl or $KMnO_4$.

(iii) Subsequent hydrolytic deprotection resulting in 2-keto-L-gulonic acid.

Extensive efforts have been made (34–38) to replace the conventional stoichiometric methods of step (ii) with the noble-metal-catalyzed air-oxidation technique. Heyns (39) was the first to suggest the direct oxidation of L-sorbose to 2-keto-L-gulonic acid. Under optimum conditions (10 wt% Pt/C catalyst, catalyst : reactant ratio (wt/wt) of 0.55, ambient temperature, pH of 7.2, and air as oxidizing agent) the yield was 61% after a reaction time of 72 h. Later, the method was investigated by several other researchers and it was found that the catalyst : reactant ratio and reaction time could be lowered substantially (40, 41). For example, 40–50% yield was obtained with a 10 wt% Pt/C catalyst after 6 h reaction time, at a pH of 7–9, 50°C, a catalyst : reactant ratio (wt/wt) of 0.2, and with oxygen as oxidizing agent (41).

Scheme 1 shows the main products of L-sorbose oxidation. For the sake of simplicity the Fisher projection of the compounds (acyclic form) is shown, but in aqueous solution at a pH of 7–8 and at near ambient temperature the pyranose configuration (glycoside form) is the most stable (42). Many possible side reactions are the reason for the moderate selectivity in the direct oxidation of L-sorbose. The formation of 5-keto-D-gluconic acid (5-KDG) and 2,5-diketo-D-gluconic acid (2,5-DKG) is due to the moderate difference in the reactivity of OH groups at the C1 and C6 atoms of L-sorbose. Oxalic acid and other aldehyde- and acid-type by-products are formed by C–C bond cleavage and by subsequent further oxidation. The presence of various by-products, which have acid–base and redox properties similar to those of 2-keto-L-gulconic acid, necessitates the use of a specific analytical method such as liquid chromatography (43, 44). Note that even in the latest studies the yield and selectivity were determined either by classical iodometric titration or by conductometric and polarographic methods, which give rather ambiguous results compared to the liquid chromatographic analysis.

The aim of the present work was to provide further evidence of the mechanism of catalyst deactivation and to elucidate the role of heavy metal promoters in the oxidation of sugar alcohols with molecular oxygen. The aqueous phase oxidation of L-sorbose to 2-KLG, described above, has been chosen as a model reaction.

EXPERIMENTAL

Catalyst Preparation

Distilled water (after ion exchange) and puriss or purum grade reagents were used for the experiments.

The promoted catalysts were prepared by modification of the following commercial catalysts: 5 wt% Pt/alumina (Engelhard, No. 7004; platinum dispersion, determined by TEM, $D = 0.30$), 5 wt% Pt/C (Engelhard, No. 4717), 5 wt% Pd/C (Doduco, No. 676-11031), 5 wt% Pd/alumina (Fluka, No. 252379,585; our code: "F"), 5 wt% Pd/alumina (Engelhard, No. 4589; our code: "E"), 10 wt% Pd/C (Montedison). A trimetallic 4 wt% Pd/1 wt% Pt/5 wt% Bi/C (Degussa, CEF 196 RA/W) catalyst was used as delivered.

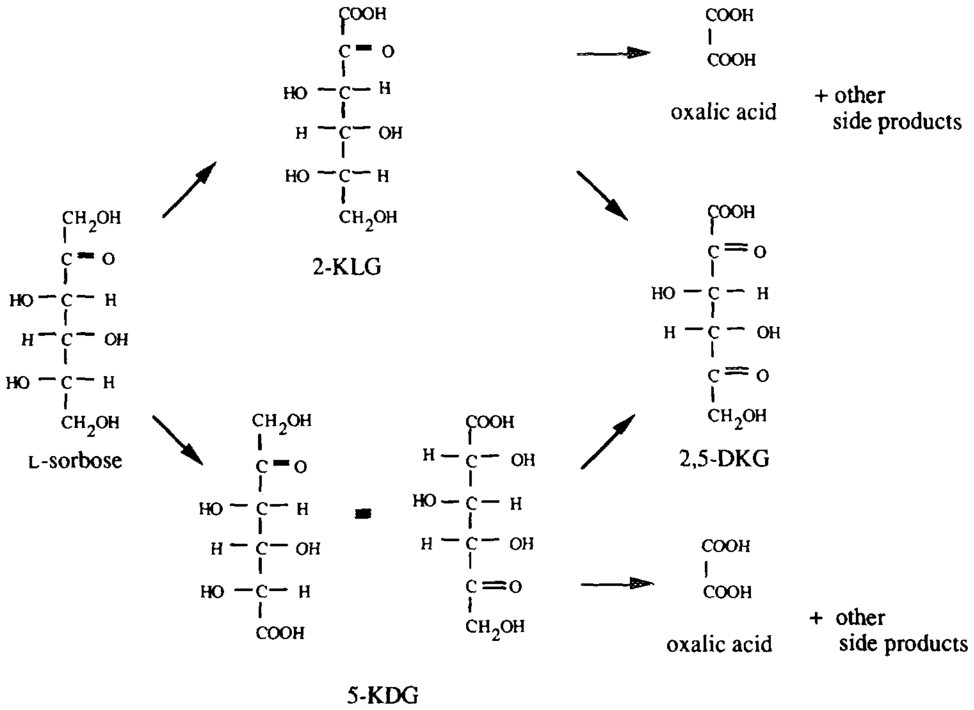
Pb and Bi deposition (modification) onto the noble metal catalyst was performed by reduction of lead acetate or bismuth nitrate with hydrogen in a dilute aqueous acidic solution (24). The catalyst was washed with 1 wt% aqueous isopropyl alcohol instead of water in order to keep the metal in a reduced state. The catalysts were dried and stored in air. Promoter: noble metal ratios in the text and figures are given as weight ratios.

Unsupported Pt powder catalyst was prepared from H_2PtCl_6 via hydroxide by hydrogen reduction (45). The Pt dispersion was 0.052 as determined from the hydrogen region of a cyclic voltammogram (46).

Oxidation Procedure

The oxidation reactions were performed in a 200-ml flat-bottom glass batch reactor (diameter 55 mm) equipped with gas distributor, condenser, combined temperature and pH electrode (Metrohm, 6.02181.010), combined potential electrode (Metrohm, 6.0415,100), and mechanical stirrer (diameter 30 mm). The temperature was controlled with a water bath within ±1°C. The air (20 ml/min) or oxygen flow rate was measured by a rotameter.

The proper amount of catalyst (catalyst/L-sorbose =



SCHEME 1

10–40 wt%), 2.0 g L-sorbose (or D-glucose), and 40 ml water were heated to the reaction temperature in a nitrogen atmosphere in order to reduce the catalyst (0.28 mol liter^{-1} initial L-sorbose concentration). The pH was adjusted from the beginning with 0.4 *M* Na_2CO_3 by automatic titration (Metrohm, 2.665.0010). The oxidation reaction was started by replacing nitrogen with air or oxygen. Samples (1 ml) of the reaction mixture were periodically taken, filtered, and stored at 5°C. The optimized conditions were pH 7.3, $T = 50°C$, $n = 1800$ rpm, $p = 1$ bar, and a catalyst: L-sorbose ratio of 0.2. These conditions were applied if not otherwise stated.

When the reaction was carried out in a controlled potential range, the oxygen content of the gas flow was regulated manually by switching between 5% O_2/N_2 and N_2.

Kinetic Measurements

The starting procedure of the kinetic measurements was the same as that described above for the oxidation reactions, and the optimal set of parameters was applied. However, the catalyst: L-sorbose ratio was reduced to 0.1 in order to reach the kinetic regime. Catalyst deactivation after a relatively high initial reaction rate makes the determination of the intrinsic reaction rate rather complicated. The initial activity was defined as being proportional to the amount of converted L-sorbose in the first 300 s (13) and below 10% conversion.

Analysis

The samples were analyzed by HPLC using a Waters liquid chromatograph (pump, 600E; autosampler, 717; UV detector, 486; RI detector, 410; and integrator, 746).

The analysis was based on a method described earlier (43, 44). The separation was carried out at 45°C on a 250 × 4.6-mm stainless-steel column slurry-packed with Aminex A-28 resin (Bio-Rad Labs) and converted to the formate form. The eluent consisted of 0.4 *M* aqueous ammonium formate at a pH of 6.5. The flow rate was 0.4 ml min^{-1} with a column pressure of 65 bar. Conversions and selectivities were obtained by application of the external standard method. The concentrations were corrected for dilution during pH-controlling and for the effect of sampling. 5-Keto-D-gluconic acid (D-xylo-5-hexulosonic acid), 2,5-diketo-D-gluconic acid (D-*threo*-2,5-hexodiulosonic acid), glycolic acid, glyoxylic acid, and oxalic acid were determined as by-products based on retention times.

Electrochemical Methods

The electrochemical cell, the modified carbon paste electrode, and the experimental setup used for cyclic voltammetric measurements have been described previously (47). In brief, 2 mg Pt or Bi/Pt catalyst powder was placed onto the surface of the flat carbon paste and dispersed on it. The speed of the rotating carbon paste electrode was 500 $\min^{-1}$. A Pt rod counter electrode and Ag/AgCl/KCl_{sat} reference electrode were used. The latter was separated from the main compartment of the cell by two diaphragms to avoid the pollution of the electrolyte by Cl^- ions. The polarizations were carried out in a 1 wt% aqueous Na-acetate (pH adjusted to 7.5) supporting electrolyte in a nitrogen atmosphere at 25°C. At first the catalyst powder was reduced electrochemically at 50 mV for 10 min. The anodic polarization was carried out at a sweep rate of 2 mV s^{-1}.

In order to measure the influence of organic residues, the Pt catalyst on the carbon paste was reduced in the electrochemical cell by an aqueous L-sorbose solution (5 wt% L-sorbose in the Na-acetate electrolyte at 40°C in a N_2 atmosphere) for 10 min; then the solution was replaced by the Na-acetate electrolyte. The anodic polarization started after the potential had been adjusted to 50 mV.

The catalyst potential during the oxidation reaction was measured with a combined electrode (Metrohm). The reproducibility of the potential measurement was ±10 mV. More details of the method can be found elsewhere (25, 48). All the potentials in the paper are referred to the reversible hydrogen electrode.

X-Ray Photoelectron Spectroscopy (XPS)

The samples were prepared by pressing the supported catalyst into an indium template. X-ray photoelectron spectra were taken with a Kratos S-800 XPS instrument (Kratos, Manchester) using Mg$K\alpha$ (1253.6 eV) radiation. The base pressure of the apparatus was $<10^{-9}$ mbar. The hemispherical analyzer was operated at a constant pass energy of 40 eV, the energy resolution being 1.0 eV (Ag $3d_{5/2}$). The energy scale was calibrated using Au $4f_{7/2}$ = 84.0 eV and the peaks were corrected to the binding energy of Al $2p$ = 74.7 eV (49) due to the charging effect of the Al_2O_3 support. The Bi $4f$ signal and the Pt $4d$ signal were used to calculate the surface concentrations. The Bi^{3+}/Pt and the Bi^0/Pt ratios were calculated from the deconvoluted peak areas of the Bi $4f$ signals and from the peak area of the Pt $4d$ signal. All peak areas have been obtained by Gaussian peak fitting.

RESULTS

Study of Reaction Parameters

Preliminary experiments. The preliminary experiments indicated a good correlation between the conversion below 20% (determined by HPLC analysis) and the amount of base added during the reaction to maintain a constant pH. Interestingly, this correlation was independent of the catalyst composition or the selectivity of the reaction. Figure 1 shows some examples of this linear correlation. The base consumption is related to the calculated, theoretical amount of base necessary to maintain a constant pH, assuming 100% selectivity toward 2-KLG. The astonishingly good correlation may formally be interpreted by the assumption that the average specific (molar) acidity of the by-products is approximately the same as that of the main product 2-KLG.

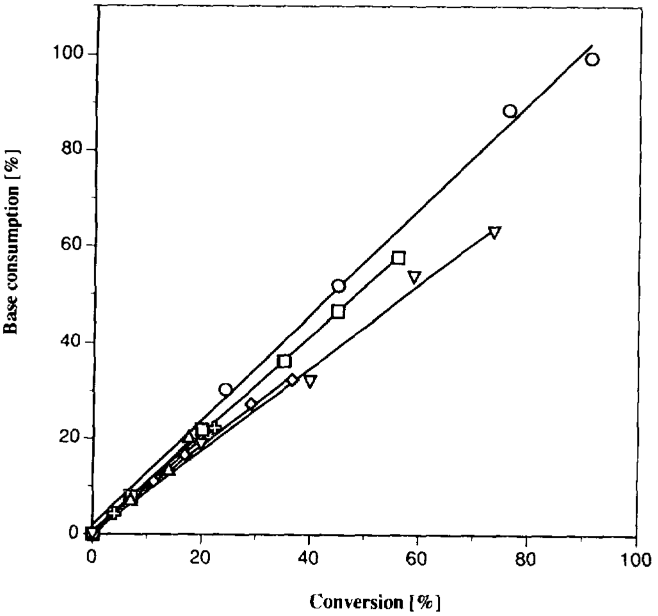


FIG. 1. Base consumption vs conversion in the oxidation of sorbose with various Pt and Pd catalysts (standard conditions): (□) 5 wt% Pt/alumina, (⊕) 10 wt% Pd/C, (△) 4 wt% Pd/1 wt% Pt/5 wt% Bi/C (Degussa), (◇) 1.5 wt% Pb/5 wt% Pt/C, (○) 5 wt% Pt/C, and (▽) 0.75 wt% Pb/5 wt% Pt/alumina.

Using the (relative) base consumption instead of the real conversion results in an error of less than 10% below 20% conversion. By applying this correlation in the kinetic experiments, the time-consuming sampling could be omitted and the experimental error of the determination of initial rates could be reduced.

In the preliminary experiments six different catalysts were used (their compositions are indicated in the legend to Fig. 1) and the influence of reaction parameters was tested. The reactions were stopped when the theoretical base consumption was reached, unless complete deactivation of the catalyst occurred before this point. The following general conclusions could be drawn from these experiments:

(i) An increase in temperature (between 40 and 75°C) or pH (between 7 and 9) increases the reaction rate but decreases selectivity to 2-KLG. At high pH the formation of polymeric by-products is also observed, especially when aqueous NaOH is used as a base instead of aqueous Na_2CO_3 (at the same, constant pH). It was found that the decomposition of the product 2-KLG was insignificant only at $T \leq 50°C$ and pH ≤ 9, which explains the low selectivity under more severe conditions.

(ii) Substitution of air by oxygen increases the reaction rate without influencing the selectivity. Other parameters, such as mixing rate or catalyst : reactant ratio, have moderate influence on the final yield.

For the optimization of quantifiable parameters (pH, temperature, etc.) the 0.75 wt% Bi/5 wt% Pt/alumina catalyst was chosen from the six catalysts tested. Note that this catalyst has been found to be the best for the partial oxidation of various primary and secondary alcohols to carbonyl compounds (26).

TABLE 1

Initial Rates of Sorbose Oxidation with Various Catalysts Containing 5 wt% Pt or Pd (Catalyst: L-Sorbose Ratio (wt/wt) = 0.1, Standard Conditions)

Catalyst	Promoter/Pt or Pd ratio (wt/wt)	Initial rate mmol min^{-1} (g cat)$^{-1}$	Prereduction by
Pt/Al_2O_3	—	0.16	L-sorbose
Pt/Al_2O_3	—	0.17	no prereduction
Pt/Al_2O_3	—	0.18	H_2
Pt/Al_2O_3	Pb/Pt = 0.15[a]	0.31	L-sorbose
Pt/Al_2O_3	Pb/Pt = 0.3	0.15	L-sorbose
Pt/Al_2O_3	Bi/Pt = 0.09	0.29	L-sorbose
Pt/Al_2O_3	Bi/Pt = 0.15	0.18	L-sorbose
Pt/Al_2O_3	Bi/Pt = 0.15[b]	0.11	L-sorbose
Pt/Al_2O_3	Bi/Pt = 0.15	0.24	H_2
Pt/C	—	0.50	L-sorbose
Pt/C	Pb/Pt = 0.1	0.60	L-sorbose
Pt/C	Pb/Pt = 0.5	0.47	L-sorbose
Pd/C	—	0.05	L-sorbose
Pd/C	Pb/Pd = 0.3	0.33	L-sorbose
Pd/Al_2O_3 "F"	—	0.12	L-sorbose
Pd/Al_2O_3 "E"	—	0.09	L-sorbose
4 wt% Pd-1 wt% Pt-5 wt% Bi/C[c]		0.19	L-sorbose

[a] Promoter : metal ratio (wt/wt).

[b] Air instead of oxygen.

[c] Commercial reference catalyst.

Optimization of reaction conditions. For the optimization procedure the reaction temperature, pH, and oxygen partial pressure were chosen as the most important parameters. In a later step the mixing efficiency and the catalyst : reactant weight ratio were also involved. The simplex optimization method (50) with randomly chosen starting points was used for the optimization. The optimized parameter was the 2-KLG yield (sorbose conversion × selectivity to 2-KLG).

The optimization indicated that with the 0.75 wt% Bi/5 wt% Pt/alumina catalyst the best yield (31%, at 78% conversion) was obtained under the following conditions: 50°C; pH 7.3; oxygen as oxidizing agent; catalyst : reactant ratio, 0.2; and mixing rate, 1800 min^{-1}. The moderate conversion is attributed to catalyst deactivation. An increase in catalyst : reactant ratio increased the final conversion slightly but decreased the selectivity to 2-KLG. If not otherwise stated, the oxidations were performed later with the optimized set of parameters, after a catalyst prereduction with L-sorbose.

Performance of selected noble metal catalysts. The initial reaction rates on selected catalysts have been determined in the kinetic regime, i.e., at high concentrations of dissolved oxygen. Under these conditions the catalysts deactivated rapidly due to overoxidation, as described in the Introduction. Nevertheless, the measurements provided some information on the initial activity with a minor distortion by the side reactions.

The initial activities of Pt and Pd on activated carbon and alumina supports are listed in Table 1. The following order of activity was found: Pt/C > Pt/alumina > Pd/alumina > Pd/C. Deactivation already occurred within the first 300 s with the Pd catalysts. In contrast to the oxidation of D-glucose (6, 7), the initial rate of L-sorbose oxidation with Pt/alumina is not influenced by the application of different starting procedures. Independent of the catalyst pretreatment (prereduction with H_2 or by L-sorbose under nitrogen, or use of air-stored catalyst without any pretreatment) similar initial rates were obtained. An explanation of this phenomenon will be given later.

The 2-KLG yield and selectivity were studied at higher conversions in an oxygen transport limited regime in order to minimize catalyst overoxidation and deactivation. The initial selectivities varied in a broad range (30–80%) and decreased with increasing conversion. In most cases the side reactions became dominant above 50% conversion, as illustrated in Fig. 2. Accordingly, the maximum in 2-KLG yield is usually reached at a partial conversion (50–80%) of L-sorbose.

The best 2-KLG yields, obtained with various supported Pt and Pd catalysts, are shown in Table 2. In most instances an early catalyst deactivation limited the final yield. This is the explanation for the low conversions characteristic of supported Pd catalysts. Higher yields have been obtained with Pt catalysts. Although Pt/C had higher initial activity (see Table 1), the final yield was higher with alumina-supported Pt. Partial reactivation of Pt catalysts was obtained by temporarily replacing the oxygen flow with nitrogen (7). However, the reactivated catalysts kept the regained activity for only a short time, and repetitive reactivation shortened the active period significantly. This behavior can be explained by successive coverage of the catalyst surface by irreversibly adsorbed by-products (51) (see later).

Note that even the best yield in Table 2 is lower than

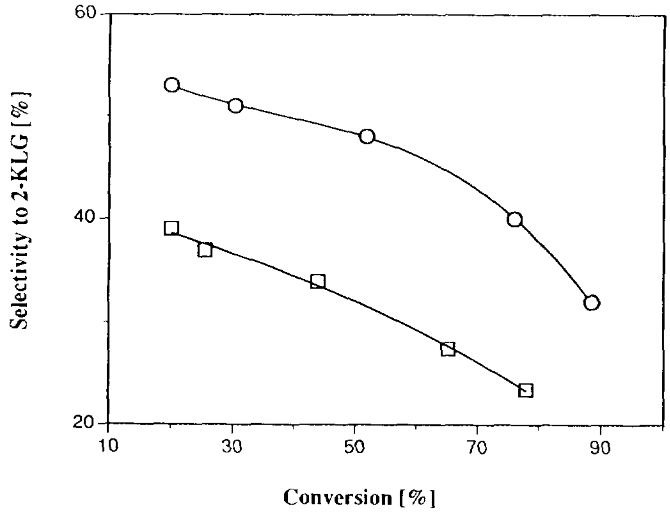


FIG. 2. Selectivity vs conversion in the oxidation of sorbose with (○) 5 wt% Pt/C and (□) 0.5 wt% Pb/5 wt% Pt/C catalyst under standard conditions.

those obtained earlier with various Pt/C and Pd/C catalysts (40, 41). One cannot exclude the possibility that all the commercial noble metal catalysts tested in this reaction have poor performance compared to those reported earlier. However, a more likely explanation is that the considerable difference between our results and literature data is due to the different reliability of the analytical methods, as has been proposed above.

Role of promotion. We tried to improve the catalytic performance of commercial Pt and Pd catalysts by Bi and Pb promotion. The initial activities and the final conversion and selectivities are shown in Tables 1 and 2, respectively. The highest initial rate was obtained with a 0.5 wt% Pb/5 wt% Pt/C catalyst. Larger amounts of lead decreased the initial rate to a level lower than that of the unpromoted catalyst, probably due to a too high coverage of Pt by Pb. Similar behavior was observed with Pt/alumina and Pd/C catalysts. Note that in the oxidation of primary and secondary alcohols there is usually an optimum at medium coverage of Pt, above which both reaction rate and selectivity decrease (25, 26).

TABLE 2

Conversions and Selectivities of Various Catalysts in L-Sorbose Oxidation (Standard Conditions)

Catalyst	Promoter/Pt or Pd ratio (wt/wt)	Time (min)	Conversion (%)	Selectivity (%)	Yield (%)
5 wt% Pt/Al_2O_3	—	172	58	67	39
5 wt% Pt/Al_2O_3	Bi/Pt = 0.09	73	65	38	25
5 wt% Pt/Al_2O_3	Bi/Pt = 0.15	135	78	39	31
5 wt% Pt/Al_2O_3	Pb/Pt = 0.15	150	62	31	19
5 wt% Pt/C	—	118	76	40	31
5 wt% Pt/C	Pb/Pt = 0.1	85	65	28	18
4 wt% Pd-1 wt% Pt-5 wt% Bi/C		95	21	31	6.5
5 wt% Pd/Al_2O_3 (E)	—	498	13	34	4.4
10 wt% Pd/C	—	140	23	28	6.4
5 wt% Pd/C	Pb/Pd = 0.3	580	33	22	7.3

In contrast to the unmodified catalysts, higher initial rates have been obtained by prereduction with hydrogen before L-sorbose is added. However, this change in the starting procedure did not extend the lifetime of the catalyst: the higher initial rate was followed by an earlier deactivation.

The selectivities obtained with modified catalysts are lower than those obtained with unmodified noble metal catalysts (Fig. 2 and Table 2). A comparison of lead and bismuth promoters indicates that with lead-modified catalysts lower yields of 2-KLG were obtained in spite of higher initial rates. The promoting effect of lead and bismuth in the L-sorbose oxidation is surprisingly small compared to that reported for the oxidation of D-glucose and lactose (16, 18). Poor results were obtained also with the commercial 4 wt% Pd/1 wt% Pt/5 wt% Bi/C catalyst, which has been found to be an excellent catalyst for the oxidation of D-glucose (16).

Concerning the overall performance of mono- and bimetallic catalysts, it can be concluded that modification of supported Pt and Pd with small amounts of lead or bismuth increases the initial rate, but, rather unexpectedly, decreases the selectivity and the maximum obtainable yield.

Nature of Catalyst Deactivation

Electrochemical measurements. In order to elucidate the nature of deactivation and the role of promoters, the oxidation state of the catalysts was measured by monitoring the catalyst potential during reaction. The course of the potential of the 5 wt% Pt/alumina catalyst during prereduction with hydrogen (8 min) and during the oxidation of L-sorbose is displayed in Fig. 3. It is seen that after the switch from hydrogen to oxygen the catalyst potential increased rapidly, indicating the oxidation of adsorbed hydrogen and subsequent OH adsorption (see later).

The base consumption is also shown in Fig. 3 as a function of reaction time. An important observation is that no base is consumed until a catalyst potential of 0.70 V has been reached. The direct correlation between base consumption and conversion at the beginning of the reaction has been addressed under Results. We can conclude that no reaction occurs below 0.70 V.

The other potential limit of the reaction was found to be 0.85 V; above this potential the oxidation of L-sorbose was practically stopped due to catalyst deactivation (over oxidation). This correlation between catalyst potential and reaction rate, which was independent of catalyst pre-

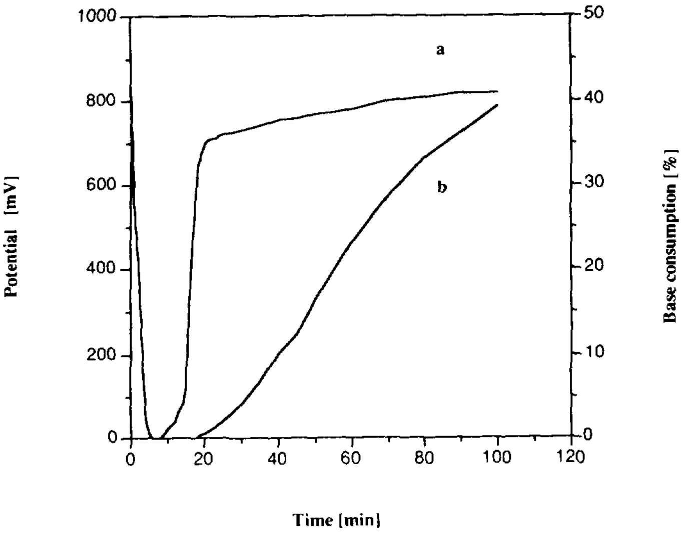


FIG. 3. Progress of catalyst potential (a) and base consumption (b) during the oxidation of sorbose with a 5 wt% Pt/Al_2O_3 catalyst. Catalyst pretreatment with hydrogen for 8 min, standard conditions.

treatment, has been found to be typical for all modified and unmodified Pt and Pd catalysts.

For the interpretation of these observations, the cyclic voltammograms of similarly prepared but unsupported Pt and Bi/Pt (Bi/Pt = 3 wt%) catalysts were measured. Unsupported catalysts were used due to the requirements of good conductivity. An electrolyte (slightly alkaline aqueous solution) as similar as possible to the reaction mixture was chosen. Only the first positive sweeps of the cyclic voltammograms were used in order to avoid the influence of restructuring (corrosion) of the samples (Fig. 4). The continuous line represents the anodic polarization of Pt. The asymmetric peak in the potential range of 0.2–0.5 V corresponds to the oxidation of adsorbed hydrogen. In the oxygen region above 0.5 V, surface oxidation of Pt by OH adsorption occurred.

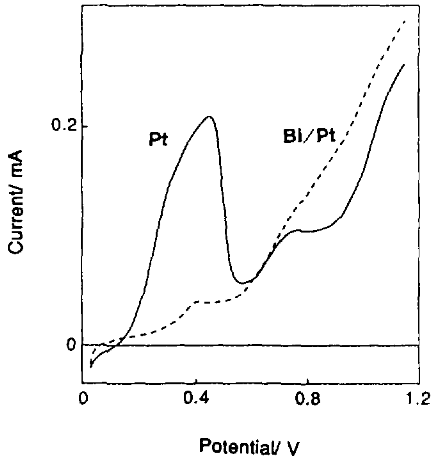


FIG. 4. Positive sweeps of the cyclic voltammogram of unsupported Pt and Bi/Pt (Bi/Pt = 0.03) catalysts in 1 wt% aqueous NaOAc at pH 7.5.

The small peak at around 0.40 V on the polarization curve of Bi/Pt, dashed line, indicates a very low hydrogen coverage in comparison with unmodified Pt. Most of the surface Pt atoms were covered by Bi adatoms, which do not adsorb hydrogen under these conditions. Partial oxidation of Bi adatoms and OH adsorption on Pt occurred in the oxygen region above 0.5 V. A detailed electrochemical interpretation of the voltammograms of Pt- and Bi-modified Pt catalysts can be found elsehwere (24, 52). Important conclusions emerging from the voltammograms are that Bi deposition onto Pt suppresses the hydrogen sorption, as expected, and that the borderline between reduced and oxidized catalyst is around 0.50–0.55 V in this slightly alkaline solution (aqueous NaOAc, pH 7.5). Note that at this pH the hydrogen and oxygen sorption on Pt partly overlap (52).

A comparison of Figs. 3 and 4 reveals that the oxidation of L-sorbose proceeds in a potential range (0.70–0.85 V) where Pt and Bi are partially oxidized. Because of this, the deactivation process cannot be due to the overoxidation of the noble metal catalysts, as is often reported in the literature (e.g., 23, 53). On the contrary, a partial oxygen coverage of Pt seems to be a necessary prerequisite of the oxidation reaction.

We proposed recently (24, 25) that catalyst deactivation during the partial oxidation of primary and secondary alcohols in aqueous alkaline medium is due to the initial destructive adsorption of the reactant on platinum. The process, termed "self-poisoning," has been widely investigated in electrocatalysis (30, 54, 57). Typical poisoning species are CO- and C_xH_y-type species. The self-poisoning process results in the overoxidation of the surface active sites, and at this higher catalyst potential the surface impurities are (partially) oxidized which increases the rate of the main reaction. We are convinced that the catalytic oxidation and the electrocatalytic oxidation of alcohols on noble metals are fundamentally similar, independent of the nature of the oxidant (electric current or molecular oxygen).

In order to prove that the overoxidation of the surface Pt atoms is not the cause but the result of deactivation, we repeated the reaction shown in Fig. 3, and at first the catalyst potential was kept between 0.40 and 0.50 V by controlling the oxygen content of the gas phase (Fig. 5). The base consumption was negligible until the catalyst potential was below 0.50 V, indicating that practically no oxidation of L-sorbose occurs until the oxygen coverage of Pt is negligible. A sudden rate enhancement was observed when pure oxygen was used again and the catalyst potential increased above 0.70 V. This is in agreement with

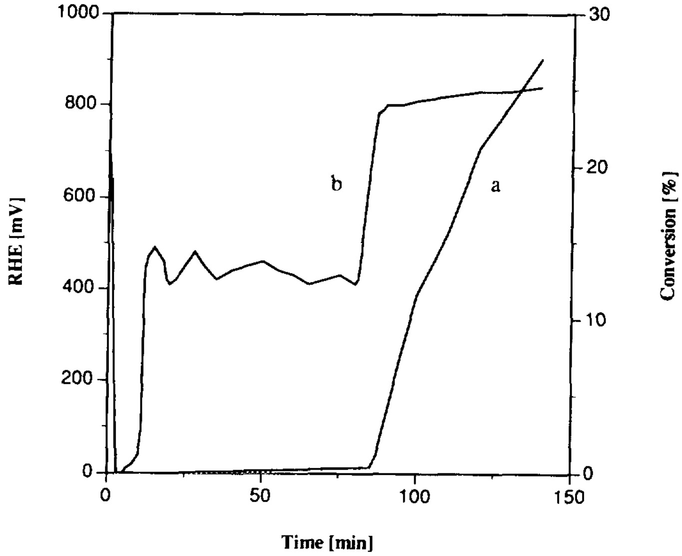


FIG. 5. Conversion of sorbose (a) and catalyst potential (b) as a functon of time of the 5 wt% Pt/Al$_2$O$_3$ catalyst. (Prereduction with hydrogen for 8 min, standard conditions.)

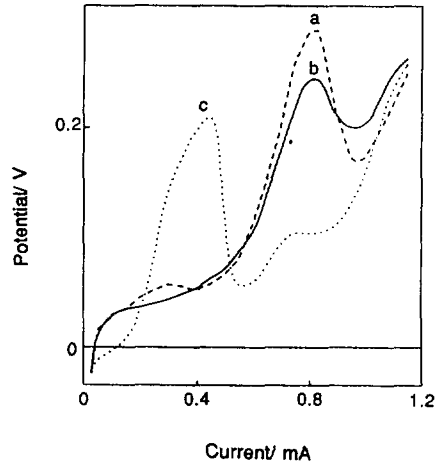


FIG. 7. Positive sweeps of cyclic voltammograms of unsupported Pt catalyst after prereduction by sorbose under N$_2$ until point "A" (a) and "B" (b) have been reached (see Fig. 6), and after reduction by hydrogen (c) in 1 wt% NaOAc at pH 7.5.

the earlier observations (27), which indicated that the oxidation of D-glucose on Pt electrodes starts above 0.60 V, i.e., at potentials where the oxidative removal of irreversibly adsorbed poisoning species renders the oxidation of D-glucose possible.

In the next series of experiments we tried to gain further information on the self-poisoning of Pt during prereduction with L-sorbose. In Fig. 6 the potential of unsupported Pt is shown during prereduction by L-sorbose under N$_2$ atmosphere in a 1 wt% aqueous NaOAc solution (pH 7.5). After the addition of L-sorbose, the measured value represents a mixed potential which is determined by two (or more) electrode processes (55, 56). The two main components are the oxygen reduction and the L-sorbose oxidation processes. At the beginning of the experiment the Pt catalyst is in an oxidized state, as it has been stored in air. During prereduction in N$_2$, Pt^{n+} is reduced to metallic Pt (Pt^0) and L-sorbose is oxidized by the oxygen-covered platinum. The former process is indicated by a fast potential drop (until point "A" in Fig. 6). Destructive "adsorption" of L-sorbose, including C–C bond cleavage and CO formation, can occur on the newly formed Pt surface. The successive coverage of Pt by poisoning species leads to an increase in the mixed potential with time (from point "A" to point "B" in Fig. 6). The same behavior has been observed with an unsupported Bi/Pt (0.03 wt% Bi) catalyst in the electrochemical cell and with the 0.75 wt% Bi/5 wt% Pt/alumina catalyst in the oxidation reactor.

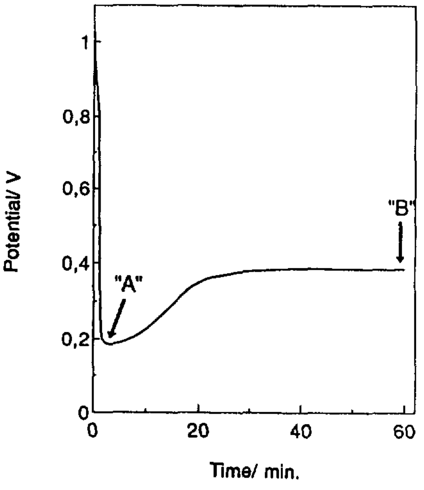


FIG. 6. Potential of unsupported Pt powder during prereduction by sorbose in N$_2$ in 1 wt% aqueous NaOAc at pH 7.5.

The cyclic voltammograms of unsupported Pt, prereduced until point "A" or "B" was reached (as shown in Fig. 6), have also been measured. The positive sweeps of the voltammograms, measured after substituting the L-sorbose-containing aqueous NaOAc solution by a sorbose-free solution, are shown in Fig. 7. In the hydrogen region below 0.5 V, there is a striking difference between the hydrogen adsorption on clean, hydrogen-reduced Pt powder (Fig. 7c) and that on the Pt prereduced by L-sorbose to point "A" (Fig. 7a). It is clear that in the latter case the majority of active sites are covered by organic species and presumably CO, preventing hydrogen sorption on Pt$_s$ atoms (27). The oxidation of these species is indicated by the peak between 0.6 and 0.9 V. Continuing the prereduction of Pt until point "B" is reached (Fig. 6), the hydrogen sorption becomes negligible (Fig. 7b). This is an indication that the destructive adsorption of

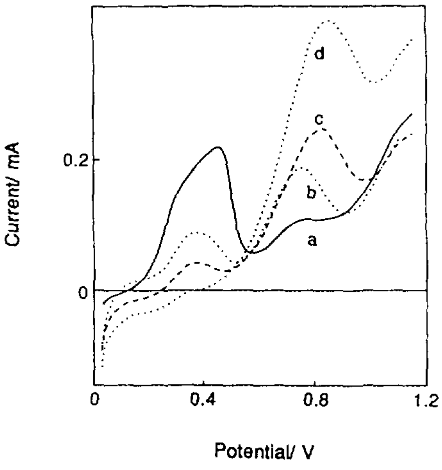


FIG. 8. Positive sweeps of the cyclic voltammogram of unsupported Pt catalyst with (a) 0.0 wt%, (b) 0.005 wt%, (c) 0.05 wt% and (d) 0.5 wt% sorbose in 1 wt% NaOAc, at pH 7.5.

the reactant proceeds with time, leading to the increased coverage of the active sites by poisoning species.

The above experiment was repeated with an unsupported Bi/Pt (3 wt% Bi) catalyst in order to reveal the role of Bi on the deactivation process. Unfortunately, an unambiguous interpretation of the results was impossible, as (i) the hydrogen sorption was too low on this catalyst and (ii) the oxidation of adsorbed organic residues and the oxidation of Bi adatoms overlapped above 0.60 V.

The studies were completed by investigating the electrochemical oxidation of L-sorbose on the same Pt catalyst and in the same, slightly alkaline aqueous solution as used above. The positive sweeps of the voltammograms (Fig. 8) indicate that the higher the L-sorbose concentration, the higher the oxidation peak around 0.80 V and the lower the amount of hydrogen adsorbed on Pt (below 0.5 V). Moreover, the oxidation of L-sorbose (Fig. 8) and the oxidation of organic residues originating from the destructive adsorption of L-sorbose (Fig. 7) take place in almost the same potential region (0.60–1.00 V)

We can conclude that the high coverage of Pt active sites by poisoning species hinders the oxidation of L-sorbose at potentials below 0.60–0.70 V. The increase in reaction rate by orders of magnitude above 0.70 V is due to the oxidative removal of poisoning species in this potential range. Note that this interpretation is in agreement with generally accepted ideas about the electrocatalytic oxidation of alcohols and carbohydrates on Pt and Pd (29–31, 57).

XPS measurements. In order to determine the surface composition of the 0.75 wt% Bi/5 wt% Pt/alumina catalyst during prereduction and L-sorbose oxidation, the following samples have been examined by XPS: (1) unused catalyst stored in air; (2) after 10 min reduction by aqueous L-sorbose under nitrogen (see Fig. 6, point "A"); (3) after 60 min reduction by aqueous L-sorbose under nitrogen (see Fig. 6, point "B"); and (4) after deactivation in L-sorbose oxidation (240 min, standard conditions). The last three samples have been filtered off, washed carefully with water, dried, and stored in air.

The XPS measurements of the first three samples showed a Pt $4d_{5/2}$ signal at 314.6 eV due to Pt^0 (58–60) and a Bi $4f_{7/2}$ signal at 158.8 ± 0.1 eV (Fig. 9) corresponding to Bi_2O_3 (61). The metallic state of Pt may be explained by the presence of organic impurities from the precursor. More details will be published elsewhere. The deconvolution of the Bi_2O_3 peak shows two distinct signals (Fig. 10), resulting in the $4f_{7/2}$ signal at 158.8 ± 0.3 eV and the Bi $4f_{7/2}$ signal (shoulder) at 156.8 ± 0.4 eV which corresponds to Bi metal (60, 62). The deactivated catalyst showed only the Pt $4d_{5/2}$ signal at 314.6 eV and the Bi $4f_{7/2}$ signal at 156.8 ± 0.4 eV.

The successive loss in the Bi-content of the catalysts during prereduction and sorbose oxidation is illustrated in Fig. 9. In comparison with the unused catalyst (curve a), the Bi surface concentration decreases considerably during the 10 min prereduction of the catalyst by L-sorbose under N_2 atmosphere (curve b). After longer reduction times (60 min, curve c) the Bi^{3+} and Bi^0 surface concentrations are even lower and after the oxidation reaction with molecular oxygen (curve d), the Bi^{3+} has almost completely disappeared from the surface. The decrease in the Bi/Pt ratio from the original value of 1.1 to a final value of 0.1 during L-sorbose oxidation indicates an almost complete loss of Bi. Note that the calculated atomic ratio of consecutively deposited Bi onto surface Pt atoms (Pt_S) is 0.5. The measured Bi/Pt ratio of 1.1 in the unused catalyst can be explained by the partial coverage of Pt by Bi, the geometry of which has been proved by a combined electron microscopic–energy dispersive X-ray analysis (24).

Despite the Bi dissolution process, the Bi^{3+}/Bi^0 ratio on the surface remains almost constant during the prereduction step. However, no further conclusion can be drawn from this ratio, as an immediate oxidation of surface Bi atoms can occur after exposure to air during filtration and drying. Nevertheless, no Bi^{3+} has been found in the used catalyst. The metallic state of Bi may be explained by irreversible adsorption of organic species on the surface Bi atoms, which prevents the oxidation of Bi^0 in air. Another possible interpretation for the stability against oxidation and corrosion of the remaining 10% Bi^0 is that this fraction represents the irreversibly adsorbed Bi adatoms on Pt. Detailed electrocatalytic studies (63, 64) revealed the unique geometric and electronic properties of this structure.

Other measurements. The XPS analysis showed that the surface Bi : Pt ratio decreases during prereduction by L-sorbose and during the oxidation reaction. However, a

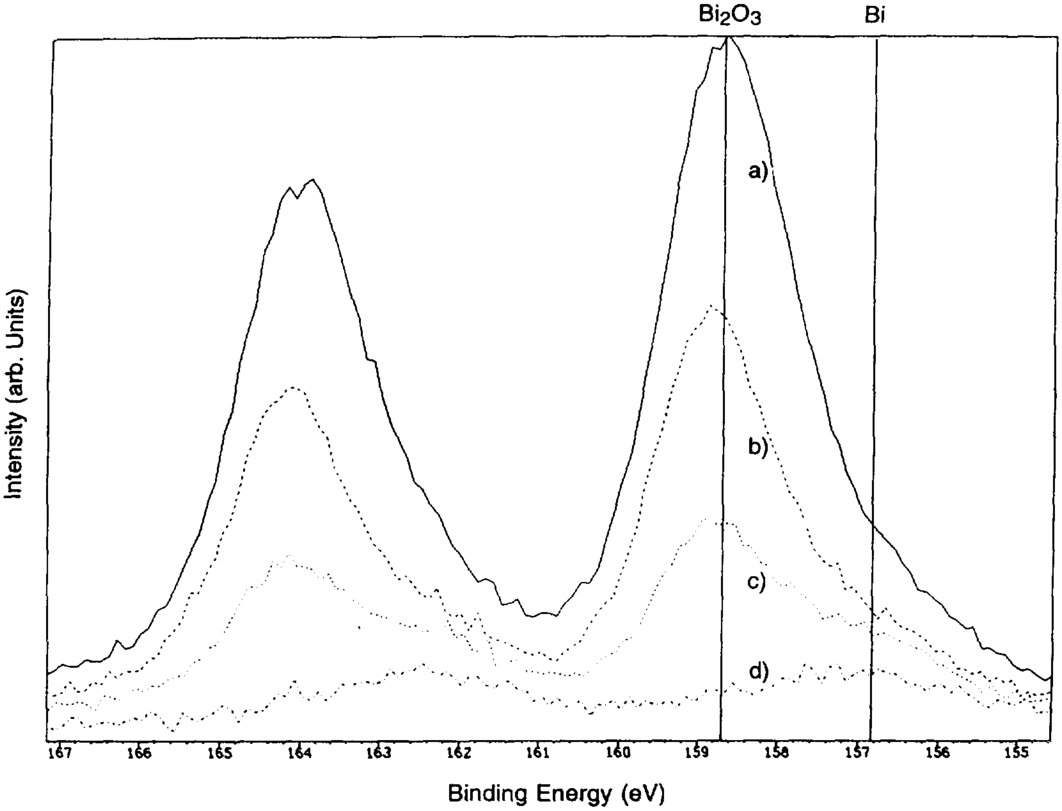


FIG. 9. XP spectra of Bi on Bi/Pt/Al_2O_3 (Bi/Pt = 0.15) catalyst. (a) unused catalyst, (b) after 10 min reduction by L-sorbose under N_2, (c) after 60 min reduction by sorbose under N_2, and (d) after use in the L-sorbose oxidation for 240 min.

change in the Pt content of the catalyst could not be unambiguously proved. A comparative analysis by means of atomic emission spectroscopy (ICP-AES) of the 0.75 wt% Bi/5 wt% Pt/alumina catalyst, before and after its use in the oxidation reaction, showed a relative loss of 8% in Pt content. This change corresponds to a 0.4 wt% loss from the original 5 wt% metal loading.

The results shown in Fig. 4 indicate that during the oxidation reaction the surface Pt atoms are in a partially oxidized state. Consequently, there is a thermodynamic possibility for Pt dissolution, similarly to Bi dissolution. XPS and ICP-AES analyses indicated a considerable difference in the rate of dissolution of Pt and Bi, as expected. Note that there was no detectable metal loss during the partial oxidation of cinnamyl alcohol to cinnamaldehyde at a pH of 10–11, using the same Bi/Pt/alumina catalyst (26). We assume that the corrosion of Bi and Pt during L-sorbose oxidation is due to the presence of sugar acids, a good chelating agent.

Transmission electron microscopy did not show any morphological difference between used and unused Bi/Pt/alumina catalysts. The regularly shaped Pt crystallites with an average diameter of 3–4 nm were comparable in the two samples. More details of the combined electron microscopy and energy dispersive X-ray analysis study of this type of catalysts have been reported elsewhere (24). It is likely that multiple reuse of the catalyst in the oxidation reaction would be necessary for obtaining detectable changes, as has been reported for the oxidation of methyl-D-glucoside on Pt/C (65).

In the field of carbohydrate oxidation most of the literature data concern the catalytic and electrocatalytic oxidation of D-glucose. In order to obtain some reference data, a comparative study of the oxidation of D-glucose and L-sorbose was performed using 5 wt% Pt/alumina and 0.75 wt% Bi/5 wt% Pt/alumina catalysts. The oxidation of D-glucose proceeded with a seven times higher initial rate, and a much slower deactivation occurred under identical conditions. The oxidation of L-sorbose and D-glucose showed a similar increase in the initial rate of 12% by Bi promotion and proceeded in the same potential range (0.7–0.85 V) independent of promotion.

From these experiments we can conclude that the moderate reaction rate and selectivity are specific features of L-sorbose oxidation and are not due to the poor performance of the commercial catalysts.

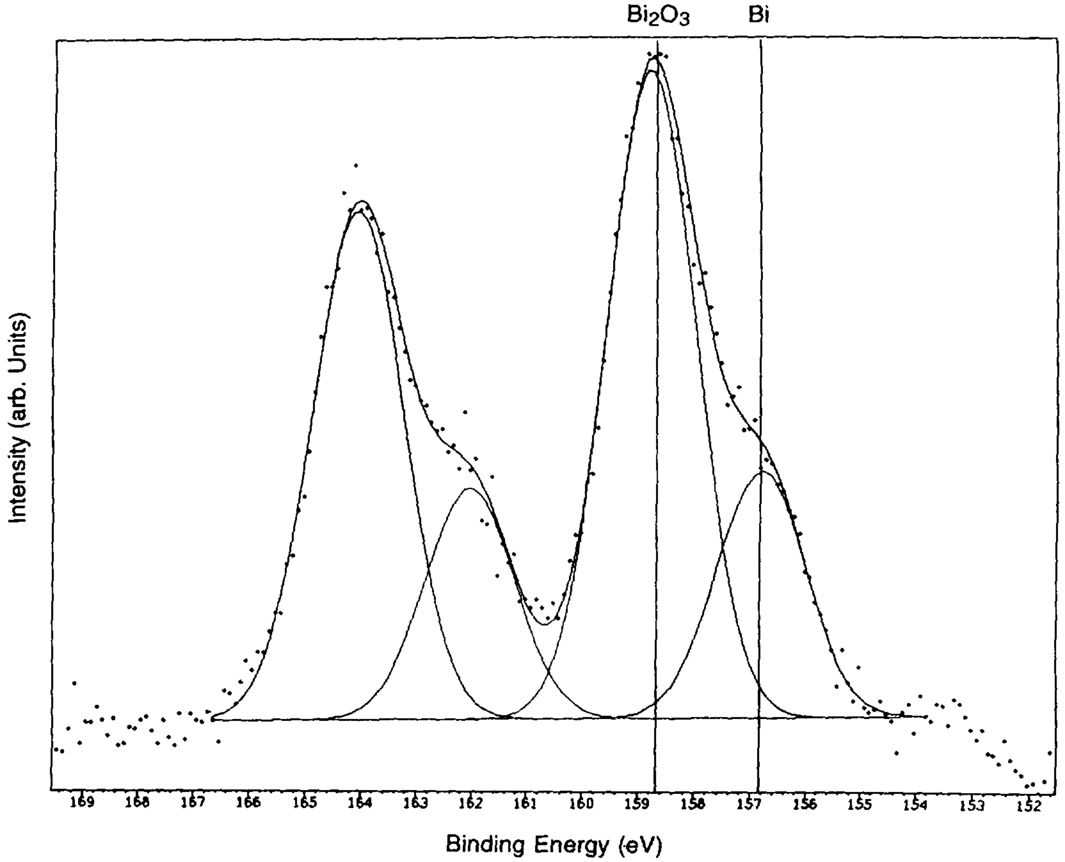


FIG. 10. Deconvolution of the XP spectra of Bi on Bi/Pt/Al_2O_3 (Bi/Pt = 0.15) catalyst after 60 min reduction by sorbose under N_2.

DISCUSSION

The use of Pt and Pd catalysts in the aqueous phase oxidation of L-sorbose to 2-KLG under optimized reaction conditions (50°C, pH 7.3, catalyst : reactant = 0.2, oxygen, n = 1800 min^{-1}) yielded moderate conversions and selectivities. The lower the pH and the temperature, the higher the selectivity and the rate of catalyst deactivation. In general, supported Pt proved to be more active and selective than corresponding Pd catalysts. Our results indicate that, despite the general use of carbon-supported catalysts in the oxidation of carbohydrates, in this reaction alumina is more suitable as a support than carbon.

We tried to improve the catalytic performance of Pt and Pd catalysts by Bi or Pb promotion. Astonishingly, the influence of promoters was limited to a moderate increase in the initial rate of reaction, and the final yield and selectivity were even lower after promotion. We could not find any indication in the literature that promotion of Pt or Pd by Bi or Pb would be detrimental in the oxidation of alcohols or polyols.

The comparative study of the oxidation of D-glucose and L-sorbose under the same conditions revealed that the poor performance of commercial catalysts (used either as delivered or after promotion) is due to deactivation problems characteristic of L-sorbose oxidation. Rather complex deactivation processes occur before and during reaction. Based on the in situ measurement of the oxidation state of the catalysts and on the XPS and ICP-AES analysis before and after sorbose oxidation, four types of deactivation can be distinguished:

(i) During the initial contact of Pt or Pd with L-sorbose a destructive adsorption of reactant occurs, resulting in the formation of CO or similarly acting species and C_xH_y-type species. Electrochemical polarization measurements provided unambiguous evidence of the presence of irreversibly adsorbed species after contact of Pt with L-sorbose.

This self-poisoning process is well known in electrocatalysis (30, 57). There is a considerable amount of *in situ* evidence for the presence of poisoning species irreversibly adsorbed on the surface Pt sites. Linearly bound CO, in addition to gluconolactone and gluconic acid, was detected on polycrystalline platinum durng the oxidation of D-glucose (27, 28). It has been proposed that CO is the major poisoning species; it is formed by catalytic decomposition of D-glucose and can be removed by oxidation above 0.6 V (RHE). This is in good agreement with our observation that the oxidation of L-sorbose proceeds in the potential range of 0.70–0.85 V. Below 0.7 V the rate of reaction was negligible.

Electrochemical polarization measurements showed that this potential range corresponds to a partially oxdized state of Pt and Bi_{ad}. (Note that it can be expected that Pd would have properties similar to those of Pt, as would Pb have to Bi, and therefore generalization of the observations is possible.) There is growing evidence for the partially oxidized state of the noble metal during alcohol oxidation (20, 24, 26). A low catalyst potential and a reduced state of the noble metal during the oxidation reaction can be expected only in those cases where no (serious) catalyst deactivation occurs. The partial oxygen coverage of Pt during reaction is not a barrier to achieving high reaction rates. Under identical reaction conditions and with the same catalyst, the reaction rate in the oxidation of D-glucose was almost an order of magnitude higher than that during sorbose oxidation.

We can conclude that the partially oxidized state of the metal surface is a consequence of self-poisoning. On the contaminated surface, the rate of sorbose oxidation is lowered and the catalyst potential (mixed potential) increases. At higher potential, the poisoning species are (partially) oxidized and removed from the surface, and the oxidation of L-sorbose may proceed at a moderate rate. The reaction, which was performed at a controlled catalyst potential below 0.5 V, proved clearly that the overoxidation of the catalyst is not the cause but the result of catalyst deactivation.

(ii) The side reactions occurring during the oxidation reaction constitute the other source of poisoning species. A broad range of by-products originating from parallel and consecutive side reactions was observed. Various small-chain aldehydes and dicarboxylic acids can be formed by breakage of the C–C bond and further oxidation. Higher pH or the use of aqueous NaOH instead of Na_2CO_3 favors aldol dimerization and polymerization. A clear indication of this type of deactivation is the early deactivation of Bi- and Pb-promoted catalysts. At the optimum promoter : noble metal ratio, the initial rate increased by a factor of 1.2–6.6, compared to the results obtained with unpromoted catalyst. However, the final conversion increased only moderately and the selectivity toward 2-KLG decreased, resulting in lower maximum yields after promotion. At higher promoter : noble metal ratios, catalyst deactivation occurred at conversions lower than those that occurred without promotion. Thus it seems that the side reactions are accelerated by the dissolved (corroded) Bi^{3+} and Pb^{2+} ions. A similar poisoning effect of Ca^{2+}, Mg^{2+}, and PO_4^{3-} ions has already been reported (1, 51).

(iii) The accumulation of poisoning species which cannot be removed oxidatively at 0.70–0.85 V (catalyst potential during reaction) results in a further increase in catalyst potential and oxygen (OH) coverage of active sites during the oxidation reaction. At ca. 0.85 V, the rate of reaction decreases to a low value due to the absence of a sufficient amount of Pt^0 or Pd^0 sites (overoxidation). It is interesting that the oxidation of L-sorbose proceeds with an acceptable rate in a rather narrow range of oxygen coverage (catalyst potential), and this potential range is approximately the same as that found during D-glucose oxidation.

(iv) The most detrimental category of catalyst deactivation is the corrosive restructuring of the catalysts. The XPS and ICP-AES measurements proved the rapid corrosion of Bi promoter (90%) and a moderate dissolution of Pt (8%) during reaction.

The corrosion of Pd/C and Pt/C catalysts in the oxidation of primary alcohols to carboxylic acids has already been reported (38, 65). According to the Pourbaix diagram (66), the corrosion of metals is strongly dependent on pH, temperature, and catalyst potential. At a pH of 7.3 (bulk) Bi can be oxidized to BiO^+ in the potential range of 0.1 to 0.9 V and can be dissolved subsequently. The corrosion stability of Bi adatoms on Pt is higher than that of bulk Bi, but there is no thermodynamic barrier for dissolution of the oxygen-covered surface metal atoms. The presence of certain anions (e.g., Cl^-, NO_3^-) or complexing agents (e.g., oxalate) can enhance the corrosion process (66). In this respect the good chelating agents sugar acids are especially dangerous.

On the basis of the above discussion we can explain an interesting observation mentioned earlier. The initial rate of L-sorbose oxidation was found to be independent of the pretreatment conditions: the same initial rate (within the experimental error) was measured after catalyst prereduction by hydrogen and by L-sorbose in nitrogen and when the catalyst was used in an oxidized form without any pretreatment. The interpretation is that before oxidation of L-sorbose, the catalyst must be reoxidized up to at least 0.7 V (partial oxygen coverage) in order to obtain measurable rates. When Pt is promoted by Bi, a prereduction by hydrogen is the proper method for preserving the structure of the bimetallic catalyst and obtaining high initial rates. However, even in this case, Bi dissolves during the oxidation reaction at 0.70–0.85 V and the rate of sorbose oxidation decreases. Thus, as soon as the partially oxidized Bi interacts with 2-KLG, a rapid corrosion process eliminates the promoting effect of the surface Bi adatoms.

ACKNOWLEDGMENTS

Financial support of this work by F. Hoffmann–La Roche AG, Switzerland, and the Kommission zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged.

REFERENCES

1. Heyns, K., and Blazejewicz, L., *Tetrahedron* **9,** 67 (1960).
2. Heyns, K., and Paulsen, H., *Angew. Chem.* **69,** 600 (1957).
3. Röper, H., *in* "Carbohydrates as Organic Raw Materials" (F. W. Lichtenthaler, Ed.), p. 267. VCH, Weinheim, 1990.
4. van Bekkum, H., *in* "Carbohydrates as Organic Raw Materials" (F. W. Lichtenthaler, Ed.), p. 289. VCH, Weinheim, 1990.
5. Vinke, P., de Wit, D., de Goede, A. T. J. W., and van Bekkum, H., *in* "New Developments in Selective Oxidation by Heterogeneous Catalysis" (P. Ruiz and B. Delmon, Eds.), Studies in Surface Science and Catalysis, Vol. 72, p. 1. Elsevier, Amsterdam, 1992.
6. Dirkx, J. M. H., and van der Baan, H. S., *J. Catal.* **67,** 1 (1981).
7. Dirkx, J. M. H., and van der Baan, H. S., *J. Catal.* **67,** 14 (1981).
8. Dirkx, J. M. H., van der Baan, H. S., and van den Broek, J. M. A. J. J., *Carbohydr. Res.* **59,** 63 (1977).
9. Heyns, K., *Justus Liebigs Ann. Chem.* **558,** 187 (1947).
10. van Dam, H. E., Kieboom, A. P. G., and van Bekkum, H., *Appl. Catal.* **33,** 361 (1987).
11. van Dam, H. E., Duijverman, P., Kieboom, A. P. G., and van Bekkum, H., *Appl. Catal.* **33,** 373 (1987).
12. Besson, M., Flèche, G., Fuertes, P., Gallezot, P., and Lahmer, F., *in* "Catalysis of Organic Reactions" (J. R. Kosak and T. A. Johnson, Eds.), p. 169. Dekker, New York, 1992.
13. Smits, P. C. C., Kuster, B. F. M., van der Wiele, K., and van der Baan, H. S., *Appl. Catal.* **33,** 83 (1987).
14. Kimura, H., Kimura, A., Kokubo, I., Wakisaka, T., and Mitsuda, Y., *Appl. Catal. Gen: A.* **95,** 143 (1993).
15. Smits, P. C. C., Kuster, B. F. M., van der Wiele, K., and van der Baan, H. S., *Carbohydr. Res.* **153,** 227 (1986).
16. Desperoux, B. M., Deller, K., and Peldszus, E., *in* "New Developments in Selective Oxidation by Heterogeneous Catalysis" (G. Centi and F. Trifirò, Ed.), Studies in Surface Science and Catalysis, Vol. 55, p. 159. Elsevier, Amsterdam, 1990.
17. Kokoh, K. B., Parpot, P., Belgsir, E. M., Léger, J-M., Beden, B., and Lamy, C., *Electrochim. Acta* **38,** 1359 (1993).
18. Hendriks, H. E. J., Kuster, B. F. M., and Marin, G. B., *Carbohydr. Res.* **204,** 121 (1990).
19. Kimura, H., Tsuto, K., Wakisaka, T., Kazumi, Y., and Inaya, Y., *Appl. Catal. A.* **96,** 217 (1993).
20. Schuurman, Y., Kuster, B. F. M., van der Wiele, K., and Marin, G. B., *in* "New Developments in Selective Oxidation by Heterogeneous Catalysis" (P. Ruiz and B. Delmon, Eds.), Studies in Surface Science and Catalysis, Vol. 72, p. 43. Elsevier, Amsterdam, 1992.
21. Hronec, M., Cvengrosova, Z., and Kizlink, J., *J. Mol. Catal.* **83,** 75 (1993).
22. DiCosimo, R., and Whiteside, G., M., *J. Phys. Chem.* **93,** 768 (1989).
23. Dijkgraaf, P. J. M., Rijk, M. J. M., Meuldijk, J., and van der Wiele, K., *J. Catal.* **112,** 329 (1988).
24. Mallat, T., Bodnar, Z., Baiker, A., Greis, O., Strübig, H., and Reller, A., *J. Catal.* **142,** 237 (1993).
25. Mallat, T., Bodnar, Z., and Baiker, A., *in* "Heterogeneous Catalysis and Fine Chemicals III, Studies in Surface Science and Catal., Vol. 78, Elsevier, Amsterdam, 1993, p. 377.
26. Mallat, T., Bodnar, Z., Maciejewski, M., and Baiker, A., "New Developments in Selective Oxidation," Studies in Surface Science and Catalysis, Vol. 82, p. 516. Elsevier, Amsterdam, 1994.
27. Bae, I. T., Xing, X., Liu, C. C., and Yeager, E., *J. Electroanal. Chem.* **284,** 335 (1990).
28. Popovic, K. D., Tripkovic, A. V., and Adzic, R. R., *J. Electroanal. Chem.* **339,** 227 (1992).
29. Popovic, K. D., Markovic, N. M., Tripkovic, A. V., and Adzic, R. R., *J. Electroanal. Chem.* **313,** 181 (1991).
30. Parsons, R., and VanderNoot, T., *J. Electroanal. Chem.* **257,** 9 (1988).
31. Léger, J. M., Hahn, F., Beden, B., and Lamy, C., *J. Electroanal. Chem.* **356,** 255 (1993).
32. Horanyi, G., *Electrochim. Acta* **37,** 2443 (1992).
33. Reichstein, T., Gruessner, A., *Helv. Chim. Acta.* **17,** 311 (1934).
34. Csürös, Z., Petró, J., Fogassy, E., and Lengyel, A., *Period. Polytech. Chem. Eng.* **18,** 155 (1974).
35. Hronec, M., Cvengrosova, Z., Stolcova, M., and Klavsky, J., *React. Kinet. Catal. Lett.* **20,** 207 (1982).
36. Csürös, Z., Petró, J., Fogassy, E., and Lengyel, A., *Period. Polytech. Chem. Eng.* **18,** 167 (1974).
37. Nondek, L., Zdarova, D., Malek, J., and Chvalovsky, V., *Collect. Czech. Chem. Commun.* **47,** 1121 (1982).
38. Hronec, M., Cvengrosovak, Z., Tuleja, J., and Ilavsky, J., *in* "New Developments in Selective Oxidation by Heterogeneous Catalysis" (G. Centi and F. Trifirò. Eds.), Studies in Surface Science and Catalysis, Vol. 55, p. 169. Elsevier, Amsterdam, 1990.
39. Heyns, K., *Ann. Chem.* **558,** 177 (1947).
40. Kim, V. I. E., Zakharova, V., and Kozhevnikov, I. V., *React. Kinet. Catal. Lett.* **45,** 271 (1991).
41. Lengyel-Meszaros, A., Losonczi, B., Petró, J., and Rusznak, I., *Acta Chim. Hung.* **97,** 213 (1978).
42. Angyal, S. J., *Adv. Carbohydr. Chem. Biochem.* **42,** 15 (1984).
43. Lazarus, R. A., and Seymour, J. L., *Anal. Biochem.* **157,** 360 (1986).
44. Blake, J. D., and Clarke, M. L., *J. Chromatogr.* **312,** 211 (1984).
45. Mallat, T., Bodnar, Z., and Baiker, A., *in* "Catalytic Selective Oxidations," (S. T. Oyama and J. W. Hightower, Eds.), ACS Symposium Series, Vol. 523, p. 308. Washington, 1993.
46. Woods, R., *in* "Electroanalytical Chemistry" (A. J. Bard, Ed.), Vol. 9, p. 1. Dekker, New York, 1976.
47. Mallat, T., Allmendinger, T., and Baiker, A., *Appl. Surf. Sci.* **52,** 189 (1991).
48. Sokolskii, D. V., "Hydrogenation in Solution," Izv. Nauka Kaz. SSR, Alma Ata. 1979. [In Russian]
49. Klein, J. C., and Hercules, D. M., *J. Catal.* **82,** 424 (1983).
50. Bayne, C. K., and Rubin, I. B., "Practical Experimental Design and Optimization Methods for Chemists," p. 128. VCH, 1986.
51. Mallat, T., Baiker, A., and Botz, L., *Appl. Catal.* **86,** 147 (1992).
52. Angerstein-Kozłowska, H., Conway, B. E., Barnett, B., and Mozota, J., *J. Electroanal. Chem.* **100,** 417 (1979).
53. Dijkgraaf, P. J. M., Rijk, M. J. M., Meuldijk, J., and van der Wiele, K., *J. Catal.* **112,** 337 (1988).
54. Leung, I-W. H., and Weaver, M. J., *Langmuir* **6,** 323 (1990).
55. Wagner, C., and Traud, W. Z., *Electrochem.* **44,** 391 (1938).
56. Koryta, J., and Dvořak, J., "Principles of Electrochemistry," p. 367. Wiley, Chichester, 1987.
57. Beden, B., Léger, J. M., and Lamy, C., *in* "Modern Aspects of Electrochemistry" (J. O'M. Bockris, B. E. Conway, and R. E. White, Eds.), Vol. 22, p. 97. Plenum, New York, 1992.
58. Shyu, J. Z., and Otto, K., *Appl. Surg. Sci.* **32,** 246 (1988).
59. Balakrishnan, K., and Schwank, J., *J. Catal.* **127,** 287 (1991).
60. Briggs, D., and Seah, M. P., "Practical Surface Analysis," Vol. 1. Wiley, Chichester, 1990.
61. Debies, T. P., and Rabalais, J. W. *Chem. Phys.* **20,** 277 (1977).
62. van Attekum, P. M. Th. M., and Trooster, J. M., *J. Phys. Metal. Phys.* **9,** 2287 (1979).
63. Szabó, S., and Nagy, F., *J. Electroanal. Chem.* **88,** 259 (1978).
64. Evans, R. W., and Attard, G. A., *J. Electroanal. Chem.* **345** 337 (1993).
65. Schuurman, Y., Kusrer, B. F. M., van der Wiele, K., and Marin, G. B., *Appl. Catal. A: Gen.* **89,** 47 (1992).
66. Pourbaix, M., "Atlas of Electrochemical Equilibria in Aqueous Solutions," National Association Corrosion Engineering pp. 358, 378, 533. Houston, 1974.