

Kinetic behaviour of electrochemical potential in three-phase heterogeneous catalytic oxidation reactions

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Abstract

Kinetic behaviour of catalyst electrochemical potential was studied during three-phase heterogeneous reaction of D-lactose oxidation. The influence of different factors on in situ measured catalyst electrochemical potential is considered. A kinetic model capable to explain transient behaviour of catalyst electrochemical potential at different conditions such as conversion, oxygen partial pressure, temperature and pH is proposed. © 2006 Elsevier B.V. All rights reserved.

Keywords: Electrochemical catalyst potential; pH effects; Pd; Aldehyde oxidation; In situ technique

1. Introduction: catalytic reactions under in situ catalyst potential control

Development of in situ techniques for chemical analysis of catalyst surfaces has been an area of intensive research over the recent years [1,2]. The majority of efforts is focused on gas phase reactions, while analysis of the state of the catalyst surface during synthesis of fine chemicals and pharmaceuticals, mainly conducted in three-phase systems, attracted less attention. An interesting technique is the measurement of electrochemical catalyst potential during a catalytic reaction [3–10]. This method was extensively utilized by the school of Sokolskii [5–9] for a variety of hydrogenation reactions and a large body of experimental data was collected over the years.

When organic reactions are carried out with heterogeneous catalysts in the presence of a polar solvent, an electrochemical double-layer is formed on the metallic surface, which charged species get balanced by an opposite charge of the metal. This charge is responsible for Nernst potential of the metal surface. During the progress of the reaction, the electrochemical double-layer is modified and the distribution of electrical charges is also modified, giving rise to electrode potential shifts.

There are several possibilities to investigate the influence of the catalyst potential value on the selectivity of a reaction. A tailor-made autoclave can be utilized for catalytic experiments, in which the catalyst metal particle suspension (stirred slurry) hit the stainless steel reactor wall imposing the electrode potential, which is then measured. The other possibility is to utilize a platinum working electrode, which acts as a model catalyst. In the latter case, the electrode potential could be controlled by a potentiostat and a classical electrocatalytic hydrogenation or oxidation could be performed.

Electrochemical potential of the catalyst reflects the situation with adsorbed species on the surface and, therefore, continuous measurements of the potential could be considered as an in situ technique.

Sokolskii classified several hydrogenation mechanisms, which obey either a simple mechanism without formation of any ionic intermediate or involvement of an ionic (electrochemical) mechanism. In the former case, at constant pH, the potential shift is governed by the change in surface hydrogen activity and is usually rather low. High values in the shift in electrochemical potential could be due to mass transfer effects, e.g. gas/liquid or liquid/solid mass transfer [11]. An ionic mechanism is operative for hydrogenation and hydrogenolysis of nitro and halogenated compounds, resulting in high values of the shift in potential, $\Delta\phi$.

More recently oxidation reactions of alcohols [12] were investigated by measuring the electrochemical potential of

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catalyst [3,4,13–17]. Liquid phase aerobic oxidation of alcohols was considered [3] to be an ideal field for the application of catalyst potential measurements. Such reactions occur in weakly basic or acidic aqueous solutions, giving a significant shift in the catalyst potential up to 850 mV [3]. It is generally accepted that the reaction takes place via a dehydrogenation mechanism which, in fact, can be splitted into several steps: i.e. dehydrogenation of the alcohol to an intermediate aldehyde with subsequent transformations to acids, followed by oxidation of adsorbed hydrogen atoms [17].

The aim of the present paper is to analyse kinetic behaviour of electrochemical catalyst potential at different reaction conditions. A kinetic model capable of describing experimentally observed kinetic regularities is presented. Lactose oxidation was chosen as an example since this reaction is industrially relevant. Lactobionic acid is a main reaction product which has antioxidative properties, and is primarily utilized in medical applications as an ingredient in preservation solutions for human organs awaiting transplantation. Lactobionic acid can also be used as an acidulant, complexing agent or antioxidant in food, pharmacy and medicine. Lactose, in opposite, is a by-product of dairy industry available in large quantities.

2. Experimental

2.1. Potential measurements

A special shaker reactor for in situ catalyst potential measurements was constructed (Fig. 1). This arrangement is an attractive alternative to stirred systems, since, first, it is convenient for catalyst potential measurements and, second, avoids appearance of stagnant zones of solution, improving gas-to-liquid mass transfer. The developed reactor consists of dry and wet compartments allowing operation at elevated pressures, since not only part of the electrode should be immersed into reaction media, but also electrodes for pH and potential measurements should be kept under the same pressure as a whole. To ensure constant composition of a gas mixture over reaction media, it is necessary to utilize a continuous gas flow through the reactor. For this purpose, a special stainless steel cooler was manufactured to separate gas from the liquid. A constant ratio between nitrogen and oxygen in the gas mixture is maintained by mass flow controllers (Brooks 5850E). The overall flow was 20 ml/min and in the majority of experiments the oxygen flow rate through the reactor was 2.5 ml/min. The stainless steel reactor walls were utilized as an electrode collector for measurements of the

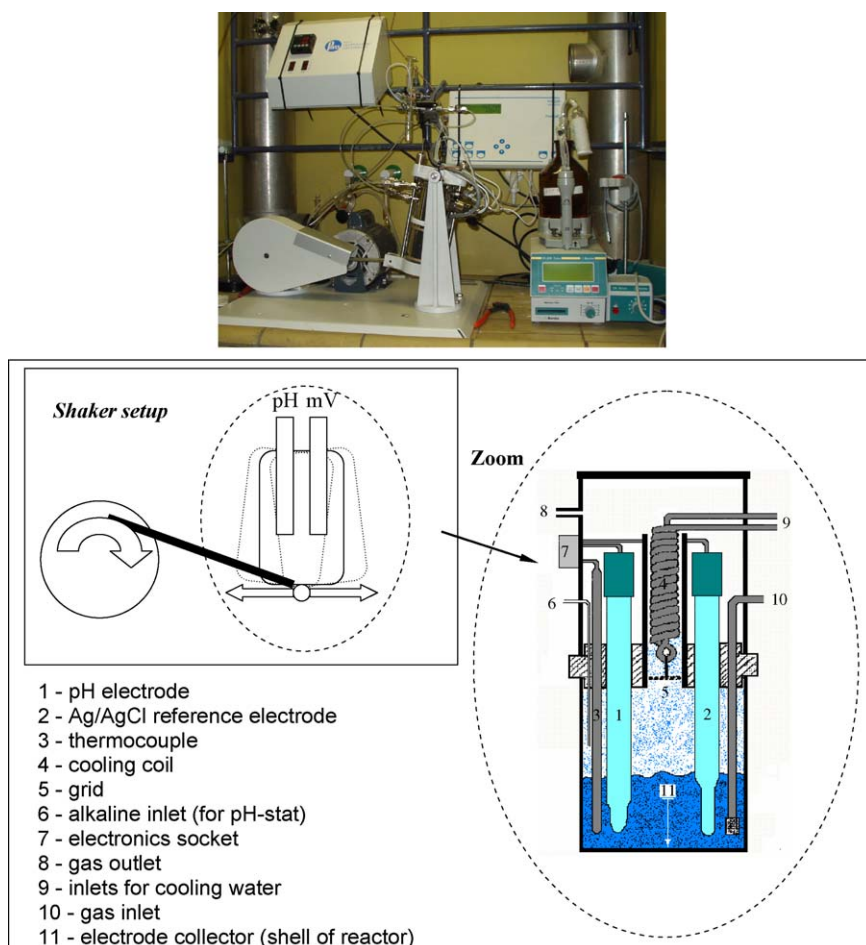


Fig. 1. Reactor set-up for catalytic experiments with in situ catalyst potential measurements.

catalyst potential. For this purpose, all parts of the reactor are electrically isolated from the shaking device (mechanical part of “3916 Hydrogenating Apparatus” Pari® with shaking frequency 4 double movements per second). Potential measurements were performed versus Ag, AgCl/3 M KCl electrode. Constant pH of reaction media was maintained by automatic titration device (Metrohm Titrino 751) at pH-stat mode by controlled addition of a 2.5 M NaOH solution.

First attempts of potential measurements were performed with a commercial Pt-ring electrode combined with a reference electrode (Radiometer MC3051Pt). It was found that the very small surface of electrode collector requires big amounts of catalyst to follow the catalyst potential. Another reason for poor results was that embedded reference electrode was not stable enough under shaking conditions. Moreover, potential measurements from stainless steel wall of a reactor are even capable of delivering the same potential value as a Pt electrode-collector [18]. The advantage of utilizing big surfaces of reactor walls is thus the possibility to perform measurements with very small amounts of catalyst (down to 50 mg per 100 g of the reaction mixture). In the latter experiments, the Pt-ring electrode was substituted by a standard Ag, AgCl/3 M KCl reference electrode (Metrohm 6.0733.100). All potentials in this article are referred to this electrode.

Catalytic experiments were performed in a semi-batch mode. After introduction of the catalyst (0.5 g, particle size < 50 μm) suspended in 72 ml of water, 100 ml of hydrogen was slowly introduced into the reactor and the catalyst was kept in contact with hydrogen, at 60 °C, for a period of 10 min. Thereafter, the reactor was flushed with nitrogen. Large concentrations of dissolved hydrogen can distort pH measurements, leading to very acidic values. Also, this can facilitate the appearance of reduction products of lactose. Consequently, after nitrogen flushing very small volume of air (less than 50 cm³) was slowly fed into the reaction vessel to consume the remaining hydrogen. After pH achieved a stable value, the rest of air was removed by nitrogen flushing. In the next step, the automatic titration for constant pH-mode was engaged and a constant pH value was adjusted. Lactose (Leprino Foods, Canada) was introduced into reactor as aqueous solution of 3.39 g of lactose monohydrate in 15 ml H₂O. In the beginning of an experiment, the overall mass of reaction mixture was 100 g and lactose concentration in the reactor typically 99.6 mmol/l. Introduction of lactose can result in almost immediate drop in pH and, therefore, pH-control should be on-line prior to this moment. After introduction of lactose, the value of potential is moving into the “hydrogen area” of the potential-

scale, indicating the reduced state of the noble metal. After the potential had reached values below –300 mV, the reaction was commenced by introduction of oxygen into the gas flow through mass flow controllers. This moment was considered as the initial starting point (0 min) of the experiments. The samples (1 ml) were periodically withdrawn from the reactor and analyzed by HPLC. The concentration evolution of the reactant, D-lactose, and the products, D-lactobionic acid sodium salt (the desired one, further denoted as LBA), 2-keto-lactobionic acid sodium salt (product of the consecutive step) as well as D-lactulose (an undesired, alkali promoted isomerization by-product) were monitored by means of high precision liquid chromatography (HPLC), equipped with a Bio-Rad Aminex HPX-87C carbohydrate column according to the method described in [19] with minor modifications (column temperature 80 °C and flow rate 0.4 ml/min were applied).

The research activities in our laboratory related to catalytic oxidation of lactose included extensive catalyst and support material screening, which is outside of the scope of the present paper and will be reported elsewhere. Some preliminary results were provided in [20].

In the present study, we are mainly concerned with kinetic behaviour of electrochemical potential and, therefore, limit our discussion mostly to Pd/C catalysts. Several commercial catalysts were applied: 5% and 10% Pd/C (Degussa) and 5% Pd/C (Aldrich) catalysts as well as the self-made 5% Pd/C [21] and 5% Pd/Al₂O₃ were tested.

To prepare a Pd (5 wt.%)/Al₂O₃ catalyst, the clean support material Al₂O₃ (La Roche) was metal-modified by incipient-wetness impregnation in a rotary evaporator (Buchi Rotavapor R114). The source of Pd was an aqueous solution of palladium(II) nitrate dehydrate (Pd(NO₃)₂·2H₂O, Fluka). Impregnated catalyst was dried overnight at 100 °C, followed by calcination in an oven at 400 °C for 2 h. The catalyst was then sieved to the particle size below 180 μm and reduced in hydrogen flow at 200 °C for 2 h. The properties of catalysts are given in Table 1.

3. Results and discussion

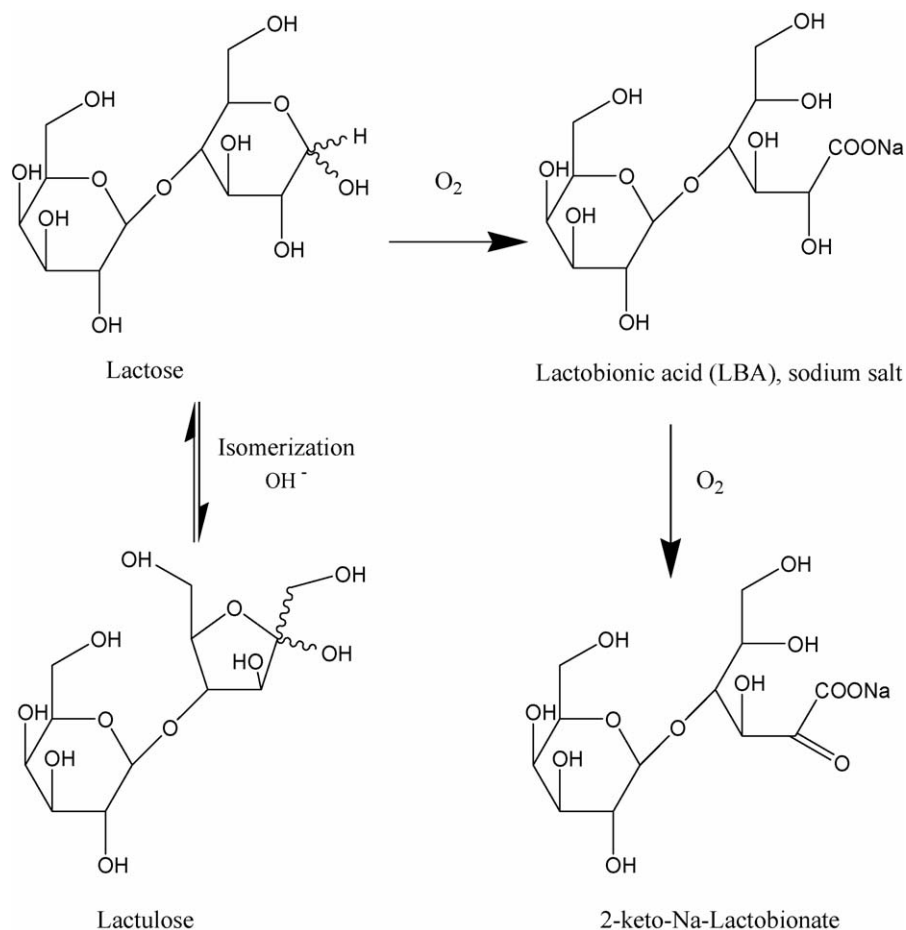
3.1. Lactose oxidation

In the present study, lactose oxidation was selected as a test reaction. During the first stage lactose transforms into lactobionic acid, and then to 2-keto-lactobionic acid, according to the Scheme 1.

Table 1
Characterization of the catalysts

Catalyst	BET surface area (m ² /g)	Dubinina surface area (m ² /g)	Dispersion (%)	Metal particle diameter (nm)*
5% Pd/C (Degussa)	715	915	29	4
5% Pd/C (Sigma–Aldrich)	936	1214	42	3
10% Pd/C (Sigma–Aldrich)	782	996	11	11
5% Pd/C (self-prepared)	399	599	23	5
5% Pd/Al ₂ O ₃ (self-prepared)	73	–	11	11

* Metal particle diameter and dispersion was measured by CO chemisorption after reduction of sample at 100 °C according to procedure described in Ref. [21].



Scheme 1. Lactose oxidation.

Oxidation of lactose is very sensitive to the composition of the adsorbed layer, in particular to such facile processes as self-poisoning or over-oxidation, as shown for instance in the case of L-sorbose [22]. For such kinds of reactions, “in situ” measured catalyst potential is an important characteristic facilitating further steps for improvement of reaction performance.

The generally accepted explanation for catalyst potential behaviour as a function of conversion presumes that when the reaction progresses, concentrations of oxidized products are increasing, lactose concentration is decreasing, the reaction slows down and unreacted oxygen moves potential into the anodic direction. It was therefore interesting to investigate the response of the electrochemical potential to the changes in oxygen concentration in the reactor. As illustrated by Fig. 2, the potential decrease from point 1 to 2 is associated with the introduction of lactose to water containing prerduced catalyst. As explained in the experimental section, first the catalyst is reduced with hydrogen, flushed with nitrogen and then exposed to lactose which drives potential to the negative direction. The following steps (denoted 3, 4, 5) show the catalyst potential response to different oxygen content in gas flow diluted by nitrogen, these being 25, 12.5, 50% of oxygen (e.g. the rates of oxygen feed were 5, 2.5 and 10 ml/min), respectively. During step 6, there is no oxygen feed into the reactor and the potential starts to move

into the cathodic direction. This means that the surface of the catalyst becomes more and more reduced with decreasing oxygen surface area coverage. To complete overall understanding of the catalyst potential phenomenon, a 50 cm³ volume of hydrogen was introduced into reactor while oxygen gas flow was stopped

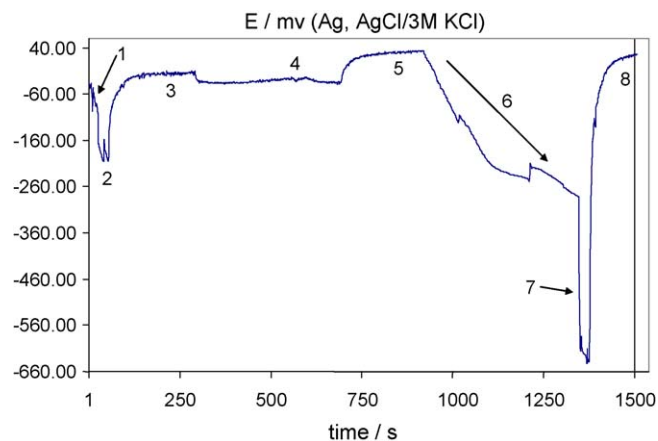


Fig. 2. Catalyst potential behaviour as a response to oxygen (hydrogen) content in gas phase during lactose oxidation over Pd (10 wt.%) / C (Aldrich) at 60 °C, pH 8.

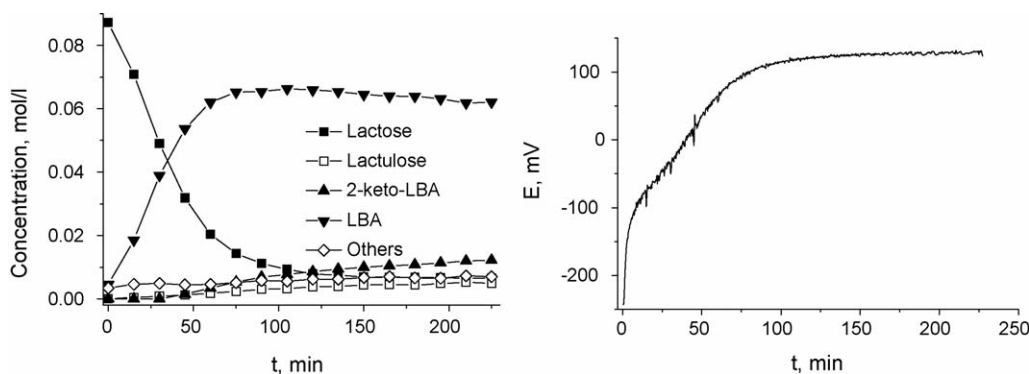


Fig. 3. Typical kinetics, and catalyst potential during oxidation of lactose over Pd (5 wt.%) /C (Degussa). Reaction conditions: 60 °C, pH 8, gas flow 20 ml/min with oxygen content 12.5 vol.%.

(Fig. 2, step 7). Hydrogen immediately reduced the catalyst surface, followed by a dramatic potential decrease. The last stage of the experiment was again the re-introduced feed of gas mixture with the oxygen content being the same as in step 5. It can be easily seen that the final levels of catalyst potential, in steps 5 and 8, also coincide.

Lactose oxidation results in acids formation corresponding to big variations in pH. It was interesting to study this reaction at different constant pH levels. Experimental data were collected within the pH range from 7 to 9. High pH values are unfavourable because of side reactions, like lactose disproportionation or coke formation, resulting into catalyst deactivation. Also at low pH values the reaction is very slow. Typical kinetic curves of D-lactose oxidation and corresponding changes of catalyst potential are presented on Fig. 3.

From the potential curve one can deduce that initially the catalyst surface was mostly covered by lactose causing reduced state of the catalyst. Introduction of oxygen changes the value of the potential dramatically. In an earlier work of Gangwal et al., significant and abrupt changes of the catalyst potential were observed during oxidation of methyl- α -D-glucopyranoside over Pt/C catalyst [17] but this was not the case in lactose oxidation.

Fig. 4 is displaying at different pH levels the product concentration versus time, as well as the catalyst potential versus

conversion. As can be seen the electrochemical catalyst potential not only increasing with conversion, but can also reach higher values at lower conversion levels (compare for instance E at conversion 50%). The reason for such behaviour is related to the fact that catalyst potential is determined by the composition of the adsorbed layer, which depends on the content of reaction mixture, e.g. concentration of oxygen and OH^- species. The detailed kinetic analysis addressing also the influence of pH will be presented later in the text.

Similar dependency was observed for Pd (5 wt.%) / Al_2O_3 catalyst (Fig. 5), where also the reaction rate increased with increase of pH (not shown).

A similar trend, e.g. increase of reaction rate with pH, was observed for oxidation of methyl- α -D-glucopyranoside over Pt/C catalyst [17], whereas potential increase in case of platinum was higher at higher pH.

Kinetic behaviour of catalyst potential at different oxygen feed rates during lactose oxidation is illustrated in Fig. 6.

From curves of lactobionic acid (LBA) formation (Fig. 6a), it is visible that in the beginning of an experiment the reaction rate is proportional to oxygen partial pressure. However, a decrease in lactose concentration makes the reaction slower, leading to accumulation of non-reacted oxygen on the catalyst surface. Time dependences of the catalyst potential (Fig. 6b)

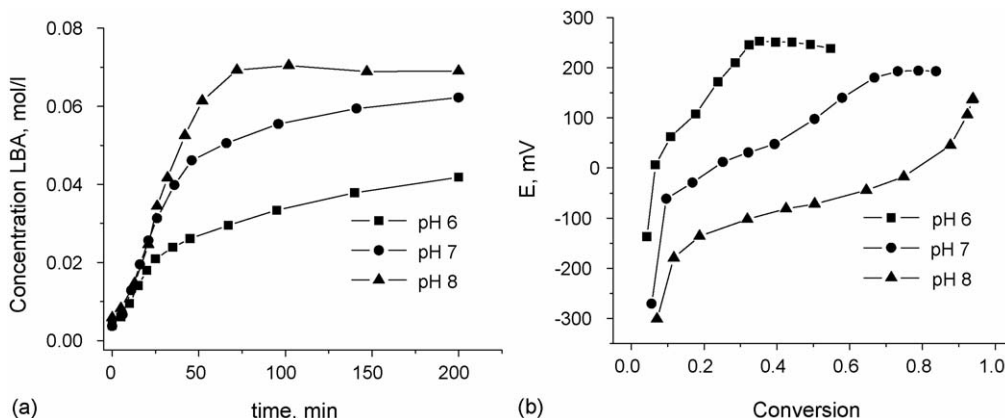


Fig. 4. Kinetic curves at different pH: (a) product concentration vs. time, (b) potential vs. conversion over Pd (5 wt.%) /C (Aldrich) catalyst at 60 °C, gas flow 20 ml/min, oxygen content 12.5 vol.%.

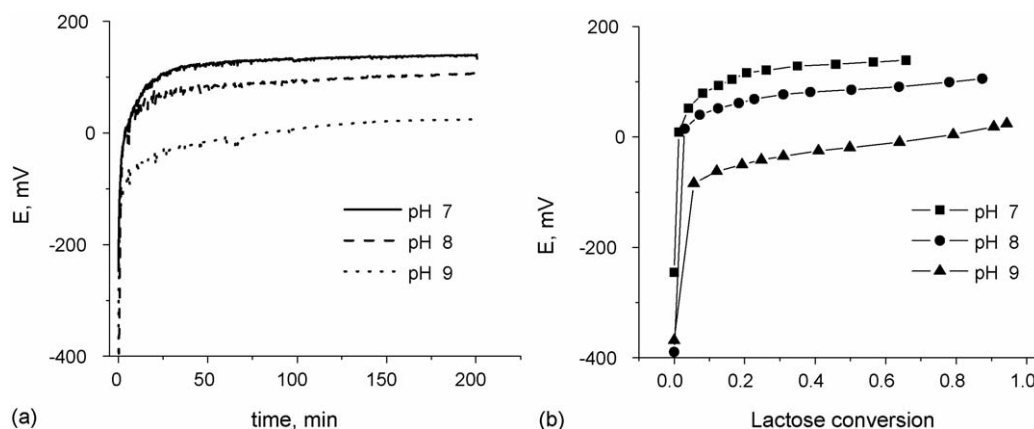


Fig. 5. Kinetic curves at different pH: (a) potential vs. time, (b) potential vs. conversion over Pd (5 wt.%) $/\text{Al}_2\text{O}_3$ catalyst at 60 °C, oxygen content 12.5 vol.%.

have linear parts with different slopes, which are characteristic for oxygen accumulation of the surfaces. The main reason for the response of catalyst potential, which reflects the energy level of the electrons during the reaction, is the transfer of electrons. This process is concomitant with changes of hydrogen and oxygen coverage on Pd surface, as will be discussed later.

Accordingly, it can be concluded that it is possible not only to measure the catalyst potential, but also to change its value by altering the rate of oxygen (hydrogen) feed. The possibility to adjust a predefined potential gives an option to perform isopotential reactions. The basis to compare isopotential reactions with electrochemical potentiostatic reactions was given by Horanyi [23]. He arrived to a very interesting conclusion, that in the case of material identity of catalytic and electrocatalytic systems, the important relationships between their various parameters should be the same. Therefore, the potential dependence of the adsorption of an organic species should be the same on a powdered platinum catalyst and on platinized platinum electrode, providing that all other conditions are the same in the two systems. This analogy, in principle, provides a possibility to use the results of electrochemical research for improvement of reaction performance over traditional heterogeneous catalysis.

Several papers were devoted to oxidation of sugars by electrochemical methods, e.g. using electrocatalytic processes on the electrode surfaces [24,25]. Such studies provide information on the reaction conditions and potentials favourable for highly selective reactions. It is well known that electrochemical reactions take place at a different potential of the working electrode. For example, it was found [25] that different stages of lactose oxidation are potential dependent. Therefore, performing the reaction at particular potentials can help to separate different stages and to avoid consecutive step of over-oxidation at highest potentials.

Industrial applications of electrochemical syntheses are very much limited by low surface area of electrodes and maintenance difficulties. Conventional noble metal electrodes display very low dispersion and, therefore, high price. These difficulties can be overcome by adjusting the catalyst potential by feeding oxygen (hydrogen), thus giving a possibility to use catalyst surface as an electrode, resulting into “electrodes” exceeding the contact area of conventional electrodes applied in electrochemistry by several orders of magnitude.

Temperature dependences of products concentration and electrochemical potentials in lactose oxidation over Pd (5 wt.%) $/\text{Al}_2\text{O}_3$ are presented in Fig. 7.

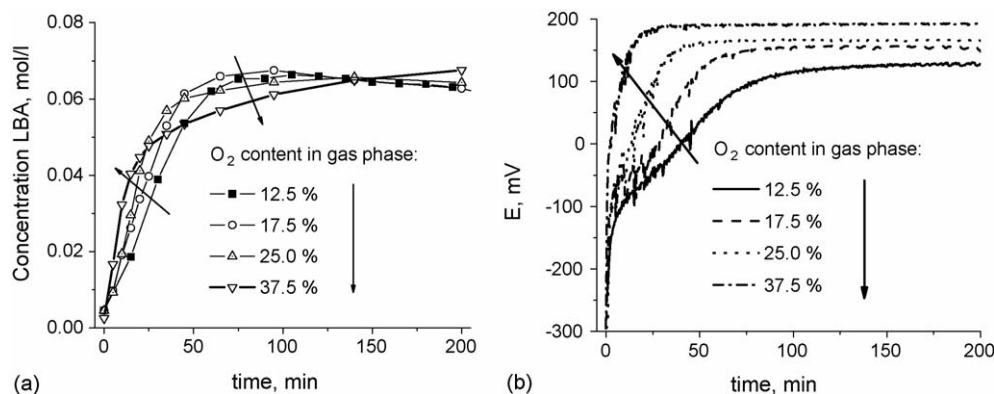


Fig. 6. Kinetic curves at different oxygen content in gas phase: (a) concentration of lactobionic acid vs. time, (b) potential vs. time, over Pd (5 wt.%) $/\text{C}$ (Degussa) catalyst at 60 °C and pH 8.

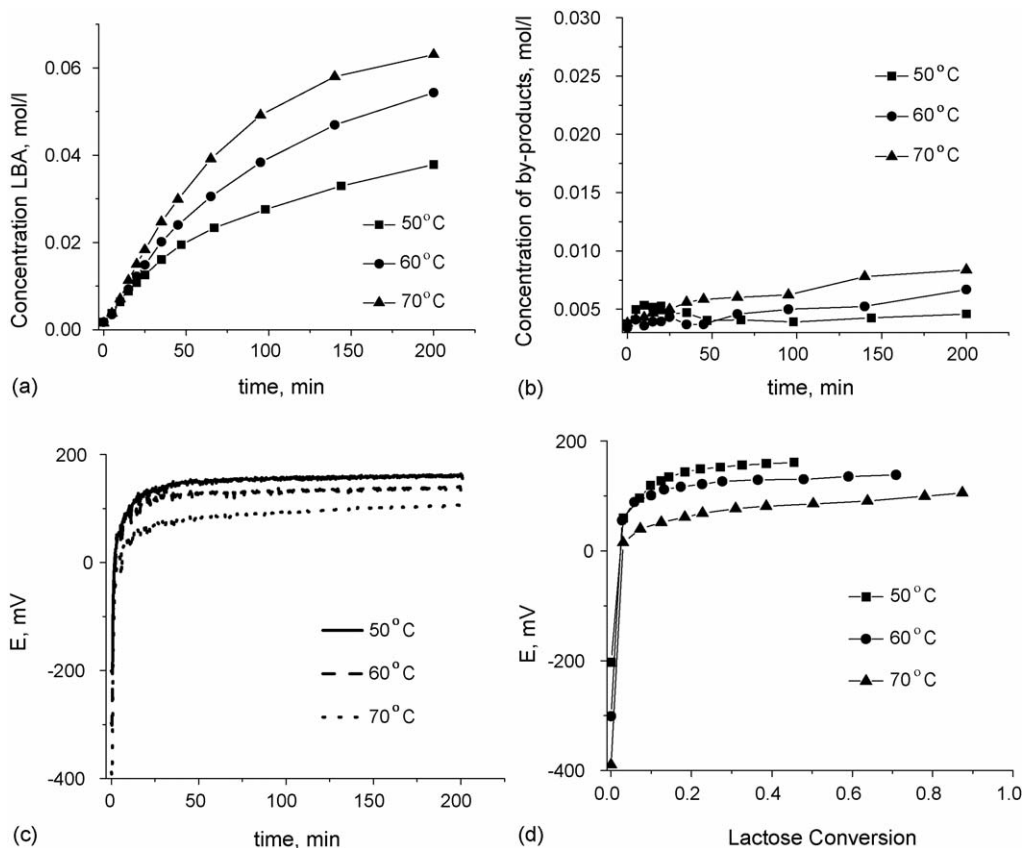


Fig. 7. Kinetic curves at different temperatures: (a) concentration of lactobionic acid vs. time, (b) concentration of by-products, (c) potential vs. time, (d) potential vs. conversion over Pd (5 wt.%) Al_2O_3 catalyst at 60°C and pH 8.

As expected, the reaction rate increased with temperature also resulting in increased by-product formation (lactulose). Like in the case of pH dependence, slower reaction rates resulted in higher values of electrode potential, at the same conversion level.

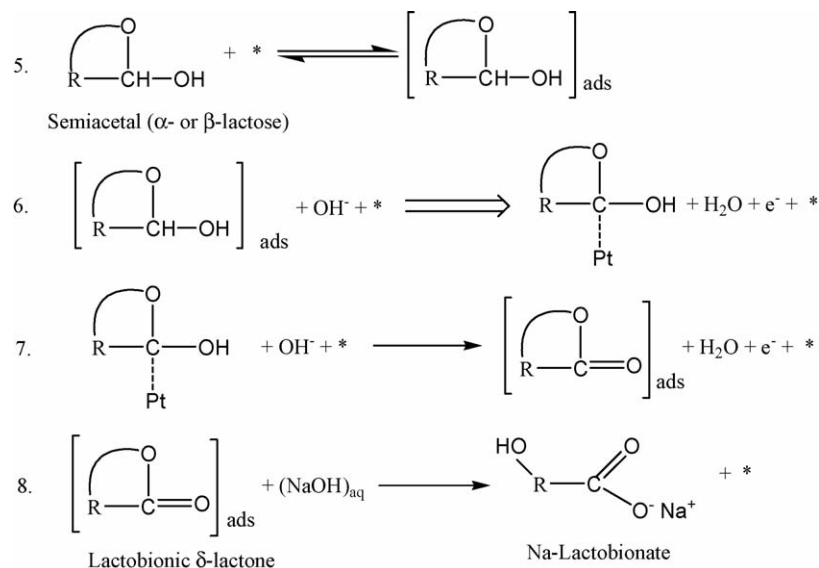
3.2. Mechanism and kinetics

Considering reactions denoted on Scheme 1, it is possible to conclude that lactose isomerization to lactulose does not play appreciable role, since its concentration is small (Fig. 3) and rate of this transformation is low compare to lactose oxidation. According to experimental results (Fig. 3), the most significant changes in the catalyst potential happen during lactose transformation to LBA (ca. 100 min for studied catalysts). From the same figure, it is visible that the rate of 2-keto LBA formation is much slower and does not affect the catalyst potential. Therefore, only the first stage of lactose oxidation is of importance for elucidating the catalyst potential behaviour.

Oxidation of aldehydes is usually described by widely accepted mechanism with the first step of an aldehyde hydration to a geminal diol and subsequent dehydrogenation leading to a corresponding acid [26]. However, lactose in water solutions is represented by two anomeric forms: α - and β -lactose differing by position of H and OH groups at carbon atom 1 in glucose residue. Substantial time is required to reach equilib-

rium for α - and β -lactose at room temperature and neutral pH. However at elevated temperatures or pH above 7.5 or below 2.5 this process is considerably accelerated [27]. It is evident that mutarotation takes place through lactose with the open glucose cycle, at the same time the open form has very low concentration being most probably on a short living mutarotation intermediate. Therefore, it can be supposed that lactose participates in the reaction not as an aldehyde, but as a semi-acetal (α - or β -lactose) which is oxidatively dehydrogenated on the metal surface giving lactobionic acid. This reaction pathway was confirmed by the presence of lactobionic acid δ -lactone as an intermediate in lactose oxidation by IR spectroscopy on Pt and Au electrodes in alkaline media [25]. It is known, however, that the reaction can also proceed in acidic media (Fig. 4). Therefore, two complimentary mechanisms of lactose oxidation could be envisaged (Schemes 2 and 3), where (*) stands for a surface site. Lactose oxidation is retarded in acidic media, which is connected to catalyst deactivation by lactobionic acid strongly adsorbed on the metal surface. Such behaviour is typical for oxidative reactions resulting in carboxylic acids formation [26].

Analysis of the transient behaviour of the electrochemical catalyst potential was reported for oxidation of an alcohol, methyl α -D-glucopyranoside [17]. Similarly to the case described in the present study alcohol oxidation involves adsorption and reduction of oxygen, dehydrogenation of alcohol (semi-acetal in case of lactose) and over-oxidation of metal surfaces. Detailed



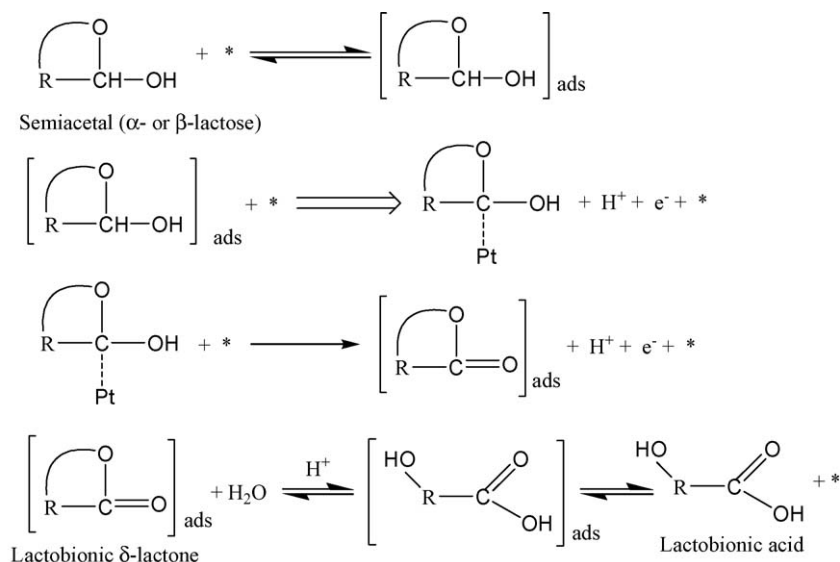
Scheme 2. Mechanism of lactose oxidation in alkaline media. Steps correspond to Eq. (1).

discussion of the various mechanistic aspects of these three steps is provided in [17].

Since lactose oxidation is more efficient in basic solutions, in the kinetic analysis given below the focus is put mainly on this reaction in alkaline media.

The sequence of steps in oxidation of lactose should include molecular adsorption of oxygen, $\text{O}_2 + * \leftrightarrow \text{O}_2^*$, as well as adsorption with dissociation $\text{O}_2 + 2* \leftrightarrow 2\text{O}^*$. Reduction of oxygen in alkaline medium involves participation of water and transfer of two $\text{O}^* + \text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons 2\text{OH}^- + *$ or four electrons $\text{O}_2^* + 2\text{H}_2\text{O} + 4\text{e}^- \rightleftharpoons 4\text{OH}^- + *$ for atomic and molecular adsorption, respectively. Hydroxyl (OH^-) species can adsorb on the catalyst surface, leading to adsorbed hydroxyls ($\text{OH}^- + * \rightleftharpoons \text{OH}^-*$). In alkaline medium such adsorption can result into formation of atomically adsorbed oxygen and

H^+ : $\text{OH}^- + * \rightarrow \text{O}^* + \text{H}^+ + 2\text{e}^-$. Protonic (H^+) species can fastly recombine with OH^- giving water. In acidic medium, adsorption of water leads to atomic oxygen $\text{H}_2\text{O} + * \rightarrow \text{O}^* + 2\text{H}^+ + 2\text{e}^-$. For the reaction to proceed, adsorption of reactant A is needed (Scheme 2, step 5). The product is formed by proton abstraction, requiring not only another vacant surface site but also OH^- species Scheme 2, steps 6, 7 with formation of LBA δ -lactone as an intermediate. Alkaline hydrolysis of adsorbed δ -lactone results in desorbed reaction product, LBA sodium salt (Scheme 2, step 8). This plausible mechanism depicted here is rather complex and is most probably not the only one. It contains, however, the main essential features of the mechanism proposed by Schouten and co-workers [17] for noble metal catalyzed aqueous phase oxidation reactions of alcohols, being extended to oxidation of semi-acetals. The mechanism can now be summa-



Scheme 3. Mechanism of lactose oxidation in acidic media.

rized and presented in the following way:

	N ⁽¹⁾	N ⁽²⁾	N ⁽³⁾	N ⁽⁴⁾
1. O ₂ +*≡O ₂ *	1	0	0	0
2. O ₂ +2*≡2 O*	0	1	0	0
3. O ₂ *+2H ₂ O+4e ⁻ ⇒4OH ⁻ +* (alkaline)	1	0	0	0
4. O*+H ₂ O+2e ⁻ ⇒2OH ⁻ +* (alkaline)	0	2	1	1
5. A+*≡A*	2	2	0	0
6. A*+OH*⇒B*+H ₂ O+e ⁻ +*	2	2	0	0
7. B*+OH*⇒C*+H ₂ O+e ⁻ +*	2	2	0	0
8. C*+(NaOH) _{aq} ⇒Na ⁺ P*+*	2	2	0	0
9. H ⁺ +OH ⁻ ⇒H ₂ O(fast)	0	0	1	2
10. OH ⁻ +*⇒O*+H ⁺ +2e ⁻ (alkaline)	0	0	1	0
11. H ₂ O+*⇒O*+2H ⁺ +2e ⁻ (neutral)	0	0	0	1
12. OH ⁻ +*≡OH*	4	4	0	0

N⁽¹⁾, N⁽²⁾: 2A+O₂+2(NaOH)_{aq}=2Na⁺P*+2H₂O, N⁽³⁾, N⁽⁴⁾, 0=0.

(1)

In the mechanism (1), the last equations the reader can find the overall chemical equations, which include only reactants and

$$E = \frac{RT}{2F} \ln \left(\frac{2k'_3 K_1 P_{O_2} + k'_4 \sqrt{K_2 P_{O_2}}}{k_{10} C_{OH^-} + k'_{11} + ((k_6 K_A K_{OH} C_L C_{OH^-}) / (1 + K_1 P_{O_2} + \sqrt{K_2 P_{O_2}} + K_A C_L (1 + k_6/k_7) + K_{OH} C_{OH^-}))} \right) \quad (10)$$

products. These equations are obtained by the addition of chemical equations of stages multiplied by stoichiometric numbers, given on the right side of equations of steps. These numbers are chosen in such a way that the overall equations contain no intermediates. A set of stoichiometric numbers of the steps producing an overall reaction equation determining a reaction route [28–30]. Routes must be essentially different and it is, consequently, impossible to obtain one route from another through multiplication by a number, although their respective overall equations can be identical.

Routes N⁽³⁾, N⁽⁴⁾ are empty ones [29] since they do not result in the formation of products. Presence of intermediates, which are not directly involved in non-empty routes, but appear in empty routes, nevertheless has essential impact on the overall kinetics.

The catalyst potential change during the reaction is determined by the rates of generated (steps 6, 7, 10 and 9) and consumed electrones (steps 3 and 4):

$$E = \frac{RT}{nF} \ln \left(\frac{2r_3 + r_4}{0.5r_6 + 0.5r_7 + r_{10} + r_{11}} \right) \quad (2)$$

where number of electrones $n = 2$. Under the steady state conditions $r_6 = r_7$ therefore in the following treatment only the rate of step 6 will be discussed, at the same time coverage of B will be taken into account ($\theta_B = (k_6/k_7)\theta_A$). The rate of steps in (2) are given by

$$r_3 = k'_3 K_1 P_{O_2} \theta_V \quad (3)$$

$$r_4 = k'_4 \sqrt{K_2 P_{O_2}} \theta_V \quad (4)$$

$$r_6 = k_6 K_A C_L K_{OH} C_{OH^-} \theta_V^2 \quad (5)$$

$$r_{10} = k_{10} C_{OH^-} \theta_V \quad (6)$$

$$r_{11} = k'_{11} \theta_V \quad (7)$$

where K_1 , K_2 are adsorption coefficients for molecularly and atomically adsorbed oxygen, respectively, K_A and K_{OH} are adsorption coefficient of reactant and hydroxyl ion, respectively, θ_V is coverage of vacant sites. Rate constants are apparent ones containing also concentration of water.

Modifying (2) and taking into account Eqs. (3)–(7) one gets

$$E = \frac{RT}{2F} \ln \left(\frac{2k'_3 K_1 P_{O_2} + k'_4 \sqrt{K_2 P_{O_2}}}{k_{10} C_{OH^-} + k_6 K_A K_{OH} C_L C_{OH^-} \theta_V + k'_{11}} \right) \quad (8)$$

From the balance equation of surface species, the coverage of vacant sites is obtained

$$\theta_V = \frac{1}{1 + K_1 P_{O_2} + \sqrt{K_2 P_{O_2}} + K_A C_L (1 + k_6/k_7) + K_{OH} C_{OH^-}} \quad (9)$$

leading finally to

The oxidation reaction rate per mole of reacted substrate is defined in the following way:

$$r = \frac{r_6}{2} = \frac{0.5k_6 K_A K_{OH} C_L C_{OH^-}}{1 + K_1 P_{O_2} + \sqrt{K_2 P_{O_2}} + K_A C_L (1 + k_6/k_7) + K_{OH} C_{OH^-}} \quad (11)$$

During the progress of the reaction, concentration of reactant decreases, therefore the third term in denominator in Eq. (10) diminishes leading to an increase of electrochemical potential. When the reactant is completely consumed, the electrochemical potential is constant and is determined by

$$E = \frac{RT}{2F} \ln \left(\frac{k'_3 K_1 P_{O_2} + k'_4 \sqrt{K_2 P_{O_2}}}{k_{10} C_{OH^-} + k'_{11}} \right) \quad (12)$$

Obviously, the potential is dependent on oxygen pressure, as illustrated by Fig. 6. The higher the oxygen partial pressure is, the higher is the value of E , also in agreement with Eq. (12).

Comparison between Eqs. (10) and (11) reveals that the rate can be independent on oxygen pressure, while E is much more dependent on it.

It was experimentally observed (Fig. 4) that the reaction rate is increasing with higher concentration of OH⁻ species, i.e. with increase of pH. As can be easily extracted from Eq. (12), an increase of pH leads to decrease of electrochemical potential in agreement with experiments.

As for the temperature dependence, the reaction rate exhibits conventional temperature dependence, while according to Eq. (10) electrochemical potential can decrease with temperature

increase, in agreement with experiments—provided that the contribution of activation energy of step 11 is dominant.

4. Conclusions

Behaviour of electrochemical catalyst potential was studied during semi-batch three-phase D-lactose oxidation over palladium catalysts at constant pH. For this purpose, a shaking reactor was constructed with the possibility to measure electrochemical potential of powder catalysts. The electrochemical catalyst potential shift during the reaction reflects the situation with adsorbed species on the surface. Oxidation of D-lactose to D-lactobionic acid is in particular sensitive to this composition due to possible over-oxidation and self-poisoning.

On the basis of the potential curves it can be stated, that initially the catalyst surface is mostly covered by lactose. The catalyst potential shifts to the positive direction as the reaction progresses. The values of electrochemical potential depend on conversion, pH, oxygen concentration in the gas phase and temperature.

The catalyst potential is balanced by the rates of generated and consumed electrons. A reaction mechanism is proposed for oxidation of lactose and the kinetic expression is derived. Experimentally observed kinetic behaviour of the catalyst potential corresponds well with the advanced model.

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