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Application of *in situ* catalyst potential measurements for estimation of reaction performance: Lactose oxidation over Au and Pd catalysts

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Abstract

Gold and palladium catalysts were successfully applied in aerobic D-lactose oxidation. Comparison between these catalysts revealed, that gold catalysts are more active and selective for the production of the first reaction product, lactobionic acid, while Pd can be of importance when the product of second consecutive reaction, 2-keto-lactobionic acid is aimed at. The electrochemical catalyst potential response was measured *in situ* applied for characterization of processes on the catalyst surfaces. Several reaction parameters were varied to study possibilities to predict catalyst deactivation from the measured catalyst potential.

Keywords: Aerobic D-lactose oxidation; Lactobionic acid; High precision liquid chromatography; Catalyst redox potential; Deactivation; 2-keto-lactobionic acid; Lactulose; Au, Pd, catalysis

1. Introduction

Catalyst electrochemical potential is a parameter which can be measured directly from a stainless reactor wall versus suitable reference electrode. Usually cheap and widespread potentiometric equipment (e.g. ordinary pH-meter) can be applied. Electrochemical catalyst potential control is an established method, developed several decades ago and applied for various hydrogenation and oxidation reactions [1–5]. At the same time the importance and abilities of *in situ* catalyst potential measurements in academic and industrial catalytic research are underestimated. This *in situ* information can be used to improve laboratory methods as well in process control of industrial reactors. Catalyst potential curves can be also used for express tests to elucidate the state of the catalyst after regeneration, since already from a shape of the curve obtained in standard conditions conclusions could be made about activity of a tested sample.

Catalyst potential is also sensitive to other reaction parameters, such as pH, temperature, feed rate of reactants [6] and stirring efficiency. The reason for such sensitivity is that the potential is related to the structure of the double layer formed on the metal surface of a catalyst [6].

The aim of the present paper is to demonstrate the possibility of a potentiometric method with respect to lactose oxidation over supported Au and Pd catalysts. The lactose oxidation is a consecutive reaction, resulting first in lactobionic acid (LBA), which is further oxidized to 2-keto-lactobionic acid (2-keto-LBA) (Scheme 1). In fact since the oxidation reaction is conducted in alkaline media (NaOH) not the free acids, but their sodium salts are formed. The given reaction scheme also includes lactulose, which appears in alkaline media due to a reversible isomerisation reaction. At conditions beneficial for oxidation, isomerisation to lactulose is relatively slow, but it gains importance when a catalyst is not active or deactivates.

2. Experimental

2.1. Experimental setup

A tailor made shaker reactor with a shaking frequency of four double movements per second was applied for *in situ* catalyst potential measurements. This reactor type is well suited for such measurements, due to high shaking frequency. Therefore, mixing is efficient resulting in elimination of stagnant zones of solution, and improved gas-to-liquid mass transfer. Detailed

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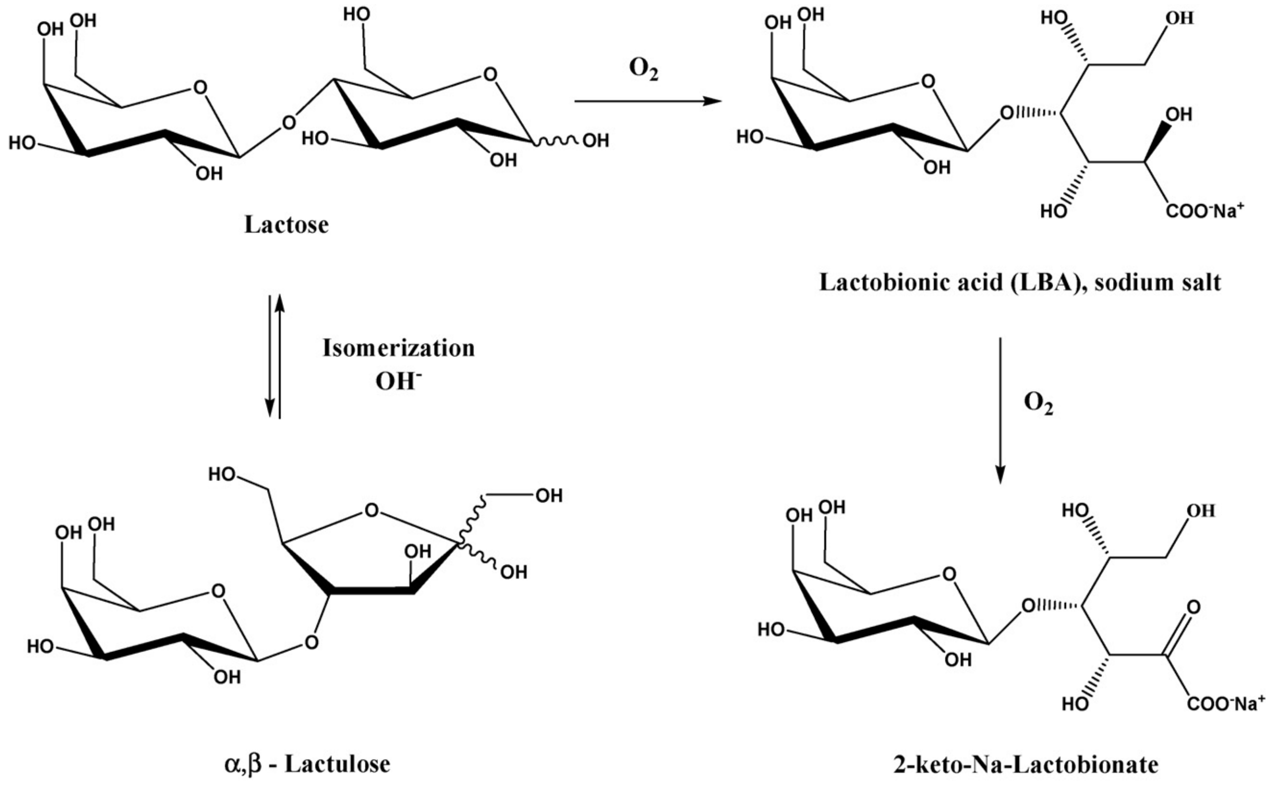

Scheme 1. The lactose oxidation scheme.

description of the setup can be found in [6]. Few pertinent details are given below. The reactor consists of dry and wet compartments making it possible to operate with pH and reference electrodes at elevated pressures. To ensure the constant composition of a gas mixture over reaction media it is necessary to use a constant gas flow through the reactor. The stainless steel reactor walls were utilized as an electrode collector for measurements of the catalyst potential. Potential measurements were performed versus Ag/AgCl/3 M KCl electrode (Metrohm 6.0733.100). All potentials in this article are referred to this electrode. It should be noted, that the walls of the reactor (stainless steel) are inert at studied conditions and do not affect the reaction. Moreover, due to lower surface area of the reactor walls compared to the catalyst surface area the changes in the electrochemical double layer of the walls can be neglected. In the absence of a catalyst (or in experiments with non-active catalysts) the measured electrochemical potential thus corresponds to oxygen dissolved in water solution of lactose.

Catalytic experiments were performed in a semi-batch mode. After introducing of the catalyst suspended in water, it was prereduced by hydrogen (AGA, 99.999%) at 60 °C for a period of 10 min. Thereafter, the reactor was flushed with nitrogen. Lactose (Leprino Foods, Canada) was introduced into the reactor as an aqueous solution. In the beginning of each experiment, the overall mass of the reaction mixture was 100 g and D-lactose concentration in the reactor was typically 99.6 mmol/l. The reaction was commenced by introduction of oxygen into the gas flow through mass flow controllers (Brooks 5850E). The pH was kept constant during the experiments by controlled addition of 2.5 M NaOH solution.

The concentration profiles of the reactant and the products were monitored by means of high precision liquid chromatography (HPLC), equipped with a Biorad Aminex HPX-87C carbohydrate column according to the method described in [7]. In experiments with consecutive runs, the catalyst was washed first with water and thereafter three times with acetone. The catalyst was then dried overnight at 60 °C. The fresh reagents were applied and the mass losses caused by reloading were taken into account in evaluation of the catalyst performance.

2.2. *Preparation of catalysts*

Two gold catalysts Au (2 wt.%)/Al_2O_3 and Au (4.7 wt.%) /Al_2O_3 were synthesized by means of a deposition-precipitation method. The support alumina (Versal VGL-25, <63 μm fraction) was precalcined (200 °C, 2 h) and then loaded with gold obtained from hydrogen tetrachloroaurate (99.9% ABCR, Darmstadt, Germany) in a following way: a slurry of deionized water and the catalyst carrier (5 g) were prepared and placed on a heating plate with magnetic stirring (450 rpm). Urea (Riedel-de-Häen, 99.5%) was added in quantities to obtain 0.21 M solution, followed by the gold precursor dissolved in a small amount of water. The temperature of the solution was set to 81 °C and mixing was continued for 24 h. Upon this procedure, urea slowly decomposes to form ammonia to facilitate immobilization and decomposition of the gold precursor on the support, resulting into small nanoclusters of Au. The pH of the solution was monitored throughout the preparation procedure and washing of the catalysts. After completed precipitation, the initially yellowish coloration of the solution disappears, indicating immobilization of the gold on the support. The catalyst was left to cool and sediment, followed by a thorough washing with deionized water until neutrality. Consequently, the catalysts were dried overnight at 60 °C in air, followed by a calcination at 200 °C for 2 h (temperature rise 2 °C/min).

To prepare a Pd (5 wt. %)/Al_2O_3 catalyst ($S_{BET} = 73\ m^2/g$, $D_{Pd} = 11\%$), the clean support material Al_2O_3 (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 ($Pd(NO_3)_2 \cdot 2H_2O$, 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.

Two samples of Pd (5 wt.%) on activated carbon were supplied by Aldrich ($S_{BET} = 936\ m^2/g$, $D_{Pd} = 42\%$) and Degussa ($S_{BET} = 715\ m^2/g$, $D_{Pd} = 29\%$).

3. Results and discussion

3.1. Catalyst potential

To discuss further information it is necessary to explain relation of catalyst potential to surface processes. Catalyst potential can be represented as a balance of steps producing and consuming electrons [6]. Initial catalyst potential depends on time that the catalyst was exposed to lactose. Adsorbed lactose dissociates on the surface with formation of adsorbed hydrogen, facilitating reduction of the metal sites. After reduction of all metal oxides, the catalyst potential is still moving to the negative direction, indicating that accumulation of adsorbed hydrogen is taking place on the surface. Therefore, there is no definitive initial potential, where the reaction starts.

Attempts to initiate reaction at high potential values, immediately after lactose introduction were unsuccessful due to low activity of the catalyst. However, attempts to get as small potential as possible did not bring any improvements. Moreover, long delays before initiation of the reaction resulted in elevated by-products (especially lactulose) formation. It can be conjectured, that lack of oxygen on the catalyst surface results in lactose disproportion to reduced and oxidized products. Moreover, hydrogen mass-transfer limited conditions during lactose hydrogenation enhance the formation of lactobionic acid (LBA) [8]. In the present study the oxidation experiments were typically started at the potential below −300 mV.

3.2. Influence of oxygen feed rate

Oxygen feed rate is one of the most important parameters in the case of platinum and palladium catalysts [5], since the reaction rate can be retarded due to lack of oxygen or due to oxygen poisoning at high oxygen feed rates. In the regime limited by oxygen mass transport the catalyst surface is reduced; the reaction rate might be slow and the catalyst could deactivate due to adsorption of carbonaceous deposits and CO. When the oxygen feed rate is high enough, it can exceed the rate of oxygen consumption in the oxidation reaction resulting in accumulation of oxygen on the surface and catalyst deactivation due to over-oxidation.

From the curves of LBA formation (Fig. 1a) it is visible that at the beginning of experiments the reaction rate is propor-

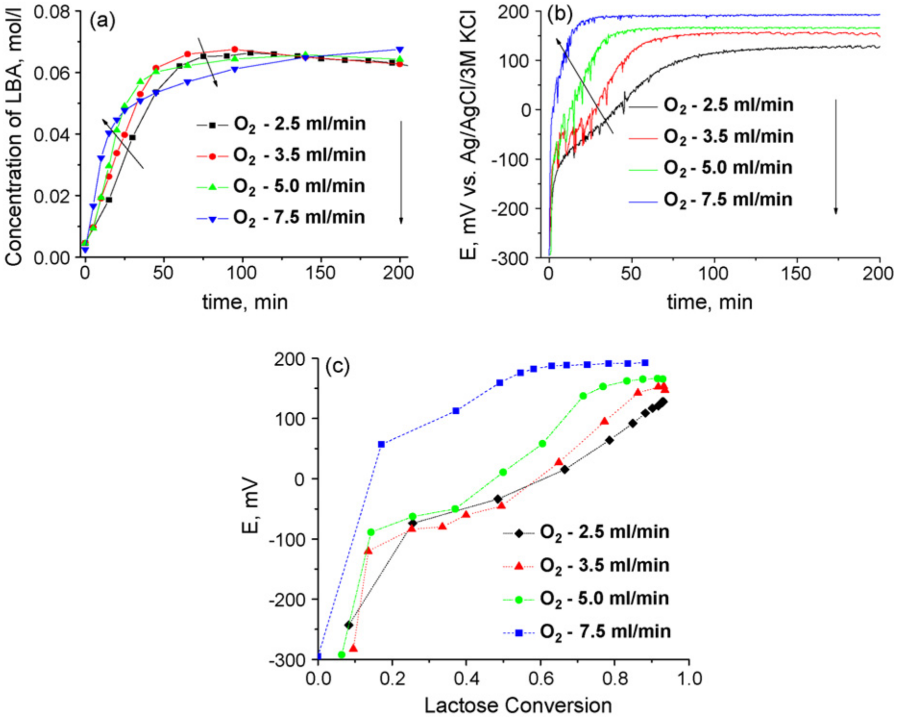

Fig. 1. Lactose oxidation over Pd (5 wt.%)/C (Degussa), $m = 0.5$ g, 60 °C and pH 8. (a) Concentration of LBA on time; (b) potential vs. time; (c) potential vs. conversion.

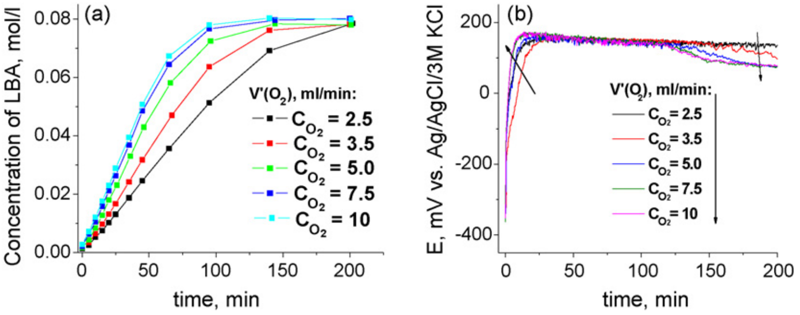

Fig. 2. The influence of oxygen feed rate on lactose oxidation over Au (2 wt.%)/Al_2O_3, $m = 0.05$ g, 70 °C and pH 8.

tional to the oxygen feed rate. However, as lactose concentration decreases, the reaction becomes slower and non-reacted oxygen accumulates on the catalyst surface. Dependences of the electrochemical catalyst potential on time (Fig. 1b) have linear parts with different slope. This slope characterizes the rate of accumulation of non-reacted oxygen on the surface. Since over-oxidation should be prevented, the surface should not be saturated with oxygen, therefore reaction must be conducted under conditions of oxygen supply control. As can be seen from Fig. 1, deactivation becomes more prominent in the case of higher oxygen feed rate.

The influence of oxygen feed rate on lactose oxidation, in case of gold catalyst, was studied over Au (2 wt.%)/Al_2O_3 (Fig. 2). It can be concluded, that the reaction rate in experiments with the oxygen feed rate in the range 2.5–5.0 ml/min is limited by the oxygen feed (Fig. 2a). For experiments with higher oxygen feed rates (i.e. 7.5 and 10 ml/min), changes in rate of LBA formation are very small pointing out that there is no lack of oxygen. The same conclusions follow from the linear parts in catalyst potential curves (Fig. 2b).

3.3. Influence of catalyst loading on catalyst potential transient behaviour

A series of experiments were performed with various catalyst loading (Fig. 3). The main idea was to elucidate the influence of gas/liquid mass transfer and to establish the optimum conditions for kinetic studies. Simultaneously, such measurements give a set of catalyst potential curves, which show oxygen accumulation processes on the surface. Oxygen accumulation on the surface (and therefore the catalyst potential) depends on the oxygen feed rate and the reaction rate. In non-limited gas–liquid mass transfer conditions, the reactor productivity is dependent on catalyst loading. Altered catalyst amount influences the overall oxygen consumption in the reactor. Therefore, different catalyst loadings, at constant oxygen feed rate, were tested in connection with elucidation of the catalyst potential behavior.

The conversion of lactose is demonstrated in Fig. 3a. All these experiments were performed with an oxygen feed rate of 2.5 ml/min. For experiments with 50, 100 and 120 mg of

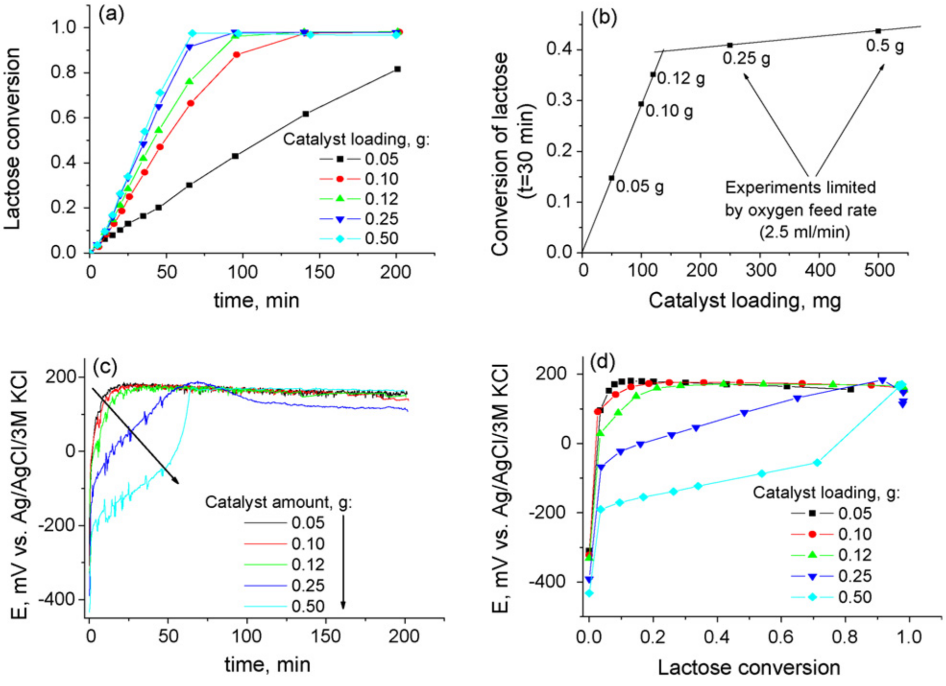

Fig. 3. Lactose oxidation with different catalyst loading over Au (2 wt.%)/Al_2O_3 at 60 °C, pH 8, oxygen feed rate 2.5 ml/min.

Au (2 wt.%) /Al_2O_3, respectively, conversion during the first 30 min is proportional to the mass of the catalyst (Fig. 3b). Further increase of the catalyst loading results in oxygen feed limited conditions (250 and 500 mg). Catalyst potential for gold at oxygen limited conditions (e.g. when oxygen mass transport is important) (Fig. 3c, 250 and 500 mg) results in linear parts in the potential dependences on time or conversion (Fig. 3d).

After the end of a batch oxygen saturates the reaction solution and the catalyst surface. It is evident that contrary to palladium, gold exhibits a different mechanism of surface oxides formation. Gold catalysts are still very active at potentials when the surface is saturated by adsorbed oxygen. From Fig. 3a it can be observed that the shortest reaction time is ca. 70 min. However, according to the catalyst potential (Fig. 3c, 0.05–0.12 g), the surface is saturated by oxygen much earlier (ca. 15 min). Interestingly, no changes of reaction rates occur at the moment, when the point of oxygen saturation is achieved (Fig. 3a). In case of Pd, when the catalyst reaches the point of oxidized potential, immediately catalyst deactivation is becoming visible (Fig. 1). Thus, it is possible to conclude, that there is no formation of catalytically inactive metal oxides in case of the gold catalysts. Linear dependences of the potential on time are obvious for Pd catalysts and, consequently successful experiments with Pd were always performed in the presence of some mass transport limitations (so-called oxygen limited conditions), since Pd deactivates when the surface is saturated with oxygen.

3.4. Influence of pH of reaction mixture

Similar to oxidation reactions of other carboxydrates [9–11] lactose oxidation is sensitive to pH of the solution. At low pH values the reaction rate is slow due to inhibition by LBA strongly adsorbed on the metal surface [6]. At high pH, lactose solution becomes yellow or even brown due to unwanted isomerization, oxidation and disproportionation. On the Fig. 4a, the concentration of LBA is shown as a function of time, at different pH values. Reaction rate is clearly enhanced at the pH range from 7 to 9. However, already at pH 9, the final LBA concentration is lower than at pH 8 due to increased amount of by-products. At pH 10 the catalyst is active during the first 10 min, then the reaction rate decreases. The final LBA concentration is almost eight times lower than at pH 8. In the Fig. 4b, the respective concentrations of by-products are illustrated.

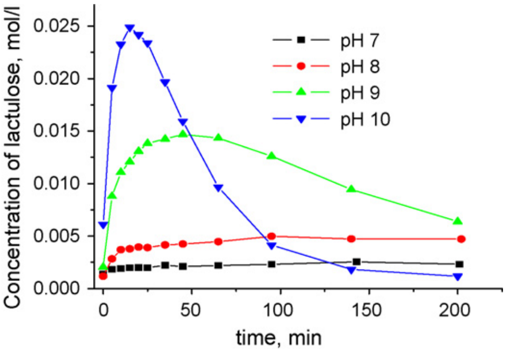

Fig. 5. Lactulose formation during lactose oxidation at different pH over Au (2 wt.%)/Al_2O_3, $m = 0.05$ g, at 70 °C, oxygen feed rate 2.5 ml/min.

As it was already mentioned earlier, lactulose formation is faster at higher pH of the lactose solution as demonstrated in Fig. 5. With the progress of the reaction, lactulose concentration stays unchanged or slowly decreases at pH range from 7 to 8. Quite substantial amounts of lactulose appear at pH ≥ 9. Lactulose concentration is then decreased which is most probably related to backward transformation to lactose.

Already from the initial part of catalyst potential dependence on time (Fig. 6a), it is possible to make certain conclusions about catalyst activity. For pH values of 7 and 9 dynamic increase of catalyst potential caused by oxygen adsorption is visible. Similar curves for Pd are characteristic for non-active catalysts, when no reaction takes place and only oxygen accumulates on the surface. Weak increase of the catalyst potential with presence of linear parts observed at pH 9 is an evidence of oxygen feed limited reaction process. Here, the most probable reason for higher by-products concentration is that side reactions, which result in disproportionation, are independent on oxygen concentration. In the case of coking, oxygen surface concentration can decrease even more due to a reaction with released hydrogen (or other reduced species). Situation with the catalyst potential is very different at pH 10. The potential is not increasing to the oxidized area and its value is oscillating. At this pH value it is can be hypothesized that fast formed coke blocks the metal surface and consumes all incoming oxygen. After all lactose was consumed by the main and side reactions ($E = -300$ mV), incoming

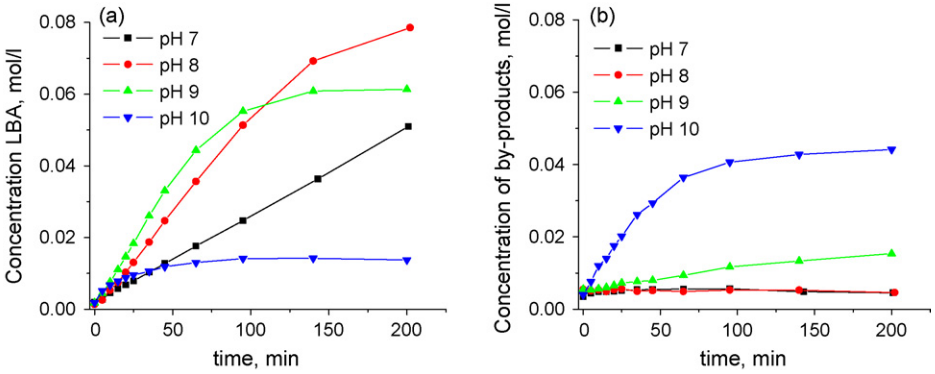

Fig. 4. Lactose oxidation at different pH over Au (2 wt.%)/Al_2O_3, $m = 0.05$ g, at 70 °C, oxygen feed rate 2.5 ml/min.

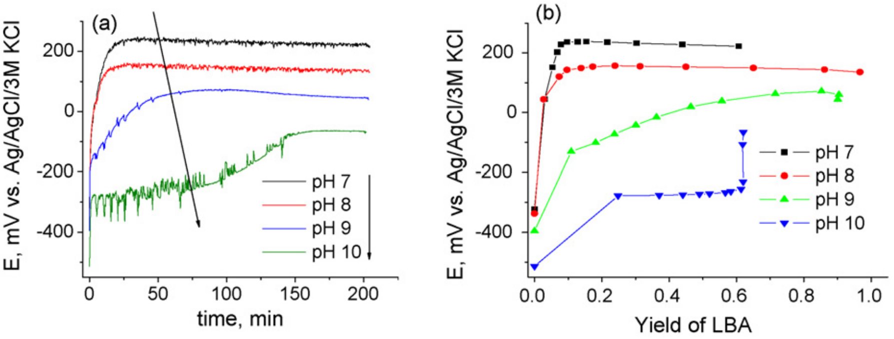

Fig. 6. Catalyst potential transient behaviour during lactose oxidation at various pH levels over Au (2 wt.%)/Al_2O_3 at 70 °C, $m = 0.05$ g, oxygen feed rate 2.5 ml/min: (a) vs. time; (b) vs. yield of LBA.

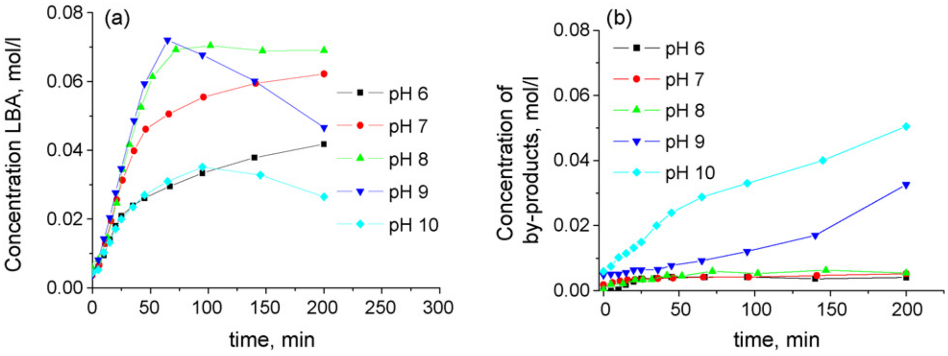

Fig. 7. Lactose oxidation at various pH values over Pd (5 wt.%)/Al_2O_3, $m = 0.5$ g, at 70 °C, oxygen feed rate 2.5 ml/min.

oxygen starts to react with less active species adsorbed on the gold surface. This is very clearly illustrated in Fig. 6b, where the yield to LBA stays constant for changes of the potential from ca. −300 to −100, thereafter oxidation of adsorbed species takes place. Removal of carbonaceous species from the metal surface results in a stable value of the potential, and the surface can be considered as regenerated by oxygen. However, it is not possible to make any conclusions about the actual metal surface area with respect to its initial value, since the catalyst potential is related to the balance of redox processes on the surface, but not to the absolute value of the surface area. The catalyst potential is independent on the total metal area and its value is a mixed potential which is a result of all redox processes on the surface [12].

Additionally to observations made with the gold catalyst, acceleration of LBA decomposition to several by-products and 2-keto-LBA takes place at elevated pH levels over palladium catalyst. This can be visible from decrease of LBA concentration (Fig. 7a). Similarly to reaction over the gold catalyst, side products deactivate palladium catalyst at pH 10 (Fig. 7b).

3.5. *Influence of temperature on lactose oxidation*

Changes observed with increase of temperature over Au (2 wt.%)/Al_2O_3 (Fig. 8) are very much similar to those obtained at different pH (Fig. 4).

Considering transient behavior of the electrochemical catalyst potential, it is possible to observe (Fig. 9) that the reaction is oxygen feed limited at 80 °C due to the fast reaction rate, and at 90 °C catalyst is deactivated: LBA concentration is not increasing after first 100 min, while amount of by-products is still increasing. Most probably coking is not as strong as in the

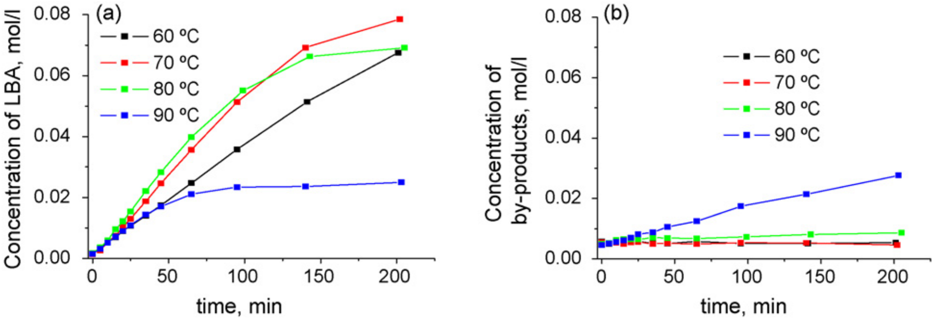

Fig. 8. The influence of temperature on lactose oxidation over Au (2 wt.%)/Al_2O_3 at pH 8, $m = 0.05$ g, oxygen feed rate 2.5 ml/min.

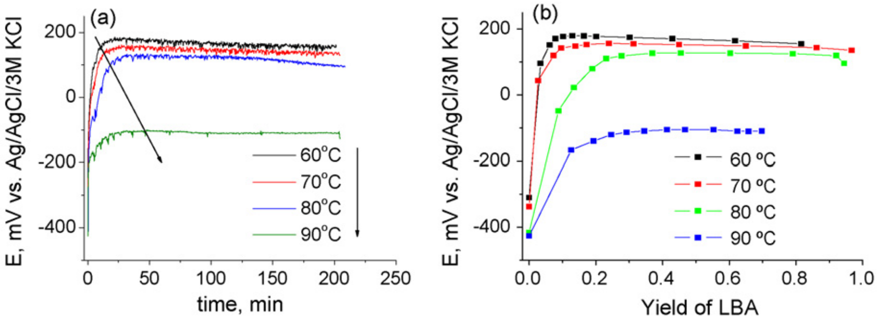

Fig. 9. Influence of temperature on the catalyst electrochemical potential during lactose oxidation over Au (2 wt.%)/Al_2O_3 at pH 8, $m = 0.05$ g, oxygen feed rate 2.5 ml/min: (a) vs. time; (b) vs. yield of LBA.

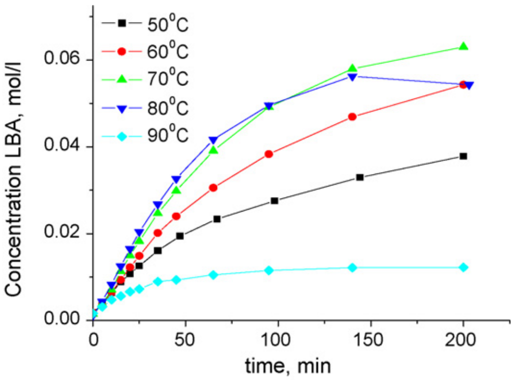

Fig. 10. The influence of temperature on lactose oxidation over Pd (5 wt.%)/Al_2O_3 at pH 8, $m = 0.5$ g, oxygen feed rate 2.5 ml/min.

case with elevated pH 10, since electrochemical potential during deactivation is more stable (compare Fig. 6a, pH 10 and Fig. 9a, 90 °C). The study of the temperature influence over Pd (5 wt.%)/Al_2O_3 gives exactly the same results (Fig. 10) indicating that deactivation process is similar over palladium and gold.

3.6. Studies of catalyst deactivation in consecutive runs

Two catalysts with similar metal loadings, Au (4.7 wt.%)/Al_2O_3 and Pd (5 wt.%)/C_{act} were used to determine the catalyst deactivation in consecutive runs. The amount of catalyst applied in the first run was 0.5 g in both cases. The experiments were performed under the following conditions: $T = 70$ °C, pH 8, and the constant oxygen feed rate 2.5 ml/min. Mass losses due to reloading of the same catalyst were taken into account by applying of special coordinate namely “mass proportional time”.

From Fig. 11 it is visible that Pd is much more prone to deactivation. Maximum selectivity towards LBA formation is higher in the case of gold. The reason for lower selectivity of palladium catalyst is the consecutive transformation of LBA to 2-keto-LBA [13].

Catalyst potentials measured during consecutive runs are shown in Fig. 12. For both catalysts, the oxidation of lactose starts with a fast increase of potential (vertical rise). This is associated with consumption of adsorbed hydrogen formed during lactose adsorption. After accumulation of substantial amounts of oxygen on the surface, the influence of reaction *per se* on catalyst potential becomes noticeable. Slower shifts of potential to more positive (oxidized) values are then observed, thus being the consequence of the increase in oxygen surface coverage. For palladium catalysts in consecutive runs the catalyst activity is decreasing, most probably due to coke formation on the surface. This process prevents adsorption of lactose, while oxygen adsorption is not hindered, which is then reflected by the fact, that in the deactivation series the electrochemical catalyst potential is more shifted towards the values, corresponding to the oxidized surfaces.

Catalyst potential behaves differently for palladium and gold catalysts (Fig. 12). Electrochemical potential of the gold catalyst reaches higher values than with palladium, followed by a decrease after the end of the reaction. This is somewhat unusual since the mixed potential during the reaction is exceeding elec-

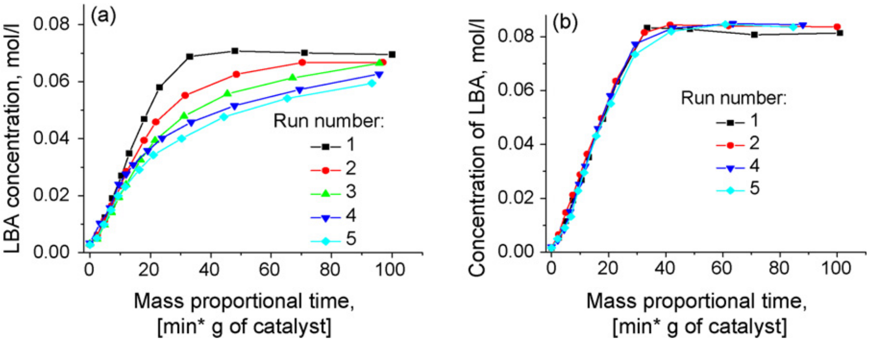

Fig. 11. Catalysts deactivation in consecutive runs: (a) Pd (5 wt.%)/C (Aldrich); (b) Au (4.7 wt.%)/Al_2O_3. Reaction conditions: $m_{cat} = 0.5$ g, $T = 70$ °C, pH 8, oxygen feed rate 2.5 ml/min.

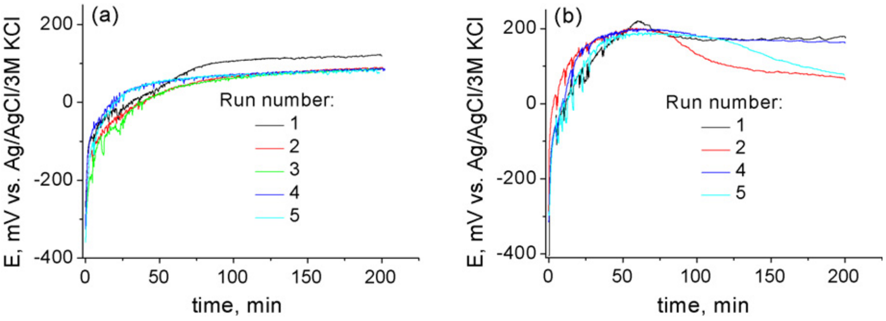

Fig. 12. Dependence of catalyst potential on time for consecutive runs: (a) Pd (5 wt.%)/C (Aldrich); (b) Au (4.7 wt.%)/ Al_2O_3. Reaction conditions: $m_{cat} = 0.5$ g, $T = 70$ °C, pH 8, $m = 0.5$ g, oxygen feed rate 2.5 ml/min.

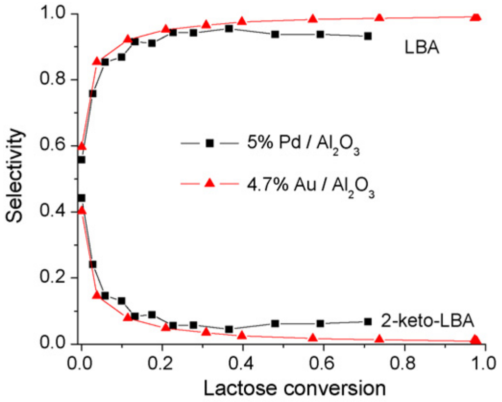

Fig. 13. Selectivity as a function of conversion for Pd (5 wt.%)/Al_2O_3 and Au (4.7 wt.%)/Al_2O_3 catalyst. Reaction conditions: $m_{cat} = 0.5$ g, $T = 60$ °C, pH 8, oxygen feed rate 2.5 ml/min.

trochemical potential of oxygen saturated surface at equilibrium (e.g. at the end of the curve). There is no clear relationship between the catalyst potential and the reaction number. A possible explanation could be that different oxygen amounts are accumulated on the surface prior to the beginning of the reaction.

3.7. Selectivity towards reaction products

A qualitative difference in the reaction products caused by the different metal nature is visible from the selectivity–conversion dependence (Fig. 13). The main feature of lactose oxidation on gold is that there is almost no formation of the product of the consecutive oxidation (2-keto-lactobionic acid).

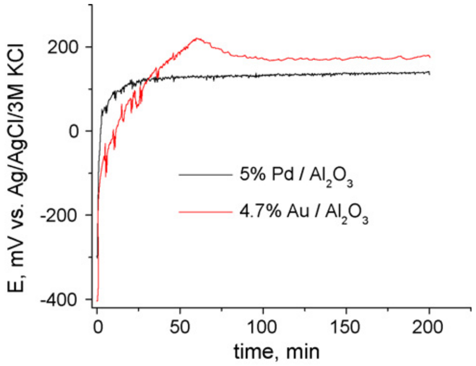

Fig. 14. Potential on time dependences for Pd (5 wt.%)/Al_2O_3 and Au (4.7 wt.%)/Al_2O_3 catalyst. Reaction conditions: $m_{cat} = 0.5$ g, $T = 60$ °C, pH 8, oxygen feed rate 2.5 ml/min.

In situ measured catalyst potential correlates well with the catalysts activity (Fig. 14).

4. Conclusions

Gold and palladium catalysts were successfully applied for lactose oxidation in a wide range of temperature, pH and oxygen feed rate with *in situ* monitoring of electrochemical catalyst potential.

The catalyst potential behaviour during lactose oxidation can be characterized by the presence or absence of linear parts, by slopes of these parts, and by the final value of the catalyst potential. Final values of catalyst potential are characteristic for chosen conditions (T, $p(O_2)$, pH) and catalytic system (i.e. metal nature). Electrochemical catalyst potential was found to be a very useful parameter for *in situ* monitoring of surface processes.

The results clearly illustrate that on gold catalysts D-lactobionic acid (sodium salt) can be obtained with high yields and selectivity. In general it can be concluded that gold is the optimum catalyst for the manufacture of lactobionic acid (LBA), while it cannot substitute Pd when the secondary product of lactose oxidation (i.e. 2-keto-lactobionic acid) is targeted.

It was found that compared to gold, Pd is more prone to deactivation due to overoxidation. Both catalysts were deactivated under conditions of high pH and high temperature. In series of consecutive experiments gold catalysts demonstrated higher durability than palladium counterparts.

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