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D-Lactose oxidation over gold catalysts

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Abstract

Various supported gold catalysts were utilized in aerobic lactose oxidation. Comparison between these catalysts revealed, that gold catalysts are sensitive to the type of support. Kinetic regularities, e.g. dependence on pH, temperature and oxygen feed rate were established. Gold catalysts were selective for the production of the first reaction product, sodium salt of lactobionic acid. The electrochemical catalyst potential response was measured "*in situ*" and then utilized in the reaction process characterization.

Keywords: Lactose oxidation; Gold catalysts; Electrochemical potential; Kinetic regularities

1. Introduction

Oxidation of an abundant disaccharide, lactose, results in lactobionic acid, which has found several applications, in particular in skin care and as a major constituent of organ preservation fluids during transplantation procedures. The latter is due to its ability to suppress tissue damage caused by oxygen radicals during organ storage and subsequent reperfusion, allowing organs to be preserved outside of the body for up to 2 days. Lactose is a by-product of dairy industry being available in large quantities. The oxidation of the disaccharide, lactose, is a consecutive reaction, resulting first in lactobionic acid, followed by a consecutive reaction product, 2-keto-lactobionic acid [1]. Since the oxidation reaction is conducted in an alkaline media (NaOH), not the free acids but their sodium salts are formed (Scheme 1).

Previously we reported [1] the possibility of selective catalytic lactose oxidation over some palladium catalysts. Since sugars oxidation is very sensitive to the composition of the adsorbed layer in the present study electrochemical catalyst potential [2,3] was measured *in situ*.

Oxidation of sugars is mainly performed over Pt and Pd catalysts [4,5]. However, over these catalysts prominent catalyst deactivation is generally reported. Oxidation of sugars, in particular monosaccharides, over gold catalysts has recently emerged as a very promising way to utilize highly active, selective and stable catalysts [6–8]. Bulk gold is normally considered to be inert in catalytic reactions. In contrast, supported gold nanoparticles have demonstrated exceptional low temperature catalytic activity in reactions such as the oxidation of carbon monoxide [9–11], which was related to the quantum size effects of the very small gold particles [12].

There are several advantages upon using gold as the catalytically active metal instead of other precious metals [13]: the cost is lower and price stability is greater. On a weight for weight basis gold is substantially cheaper and considerably more plentiful than platinum. However, improvements in the gold catalysts preparation are needed. For instance, financially viable catalyst preparation should be based on complete removal of precious metal from liquid phase and some techniques fail in this regard. It is well-known that the deposition–precipitation technique produces highly active catalyst but consumes large quantities of water and the cost of the waste water treatment is an expensive additional process step. Thus, other synthesis techniques should emerge to produce active catalysts.

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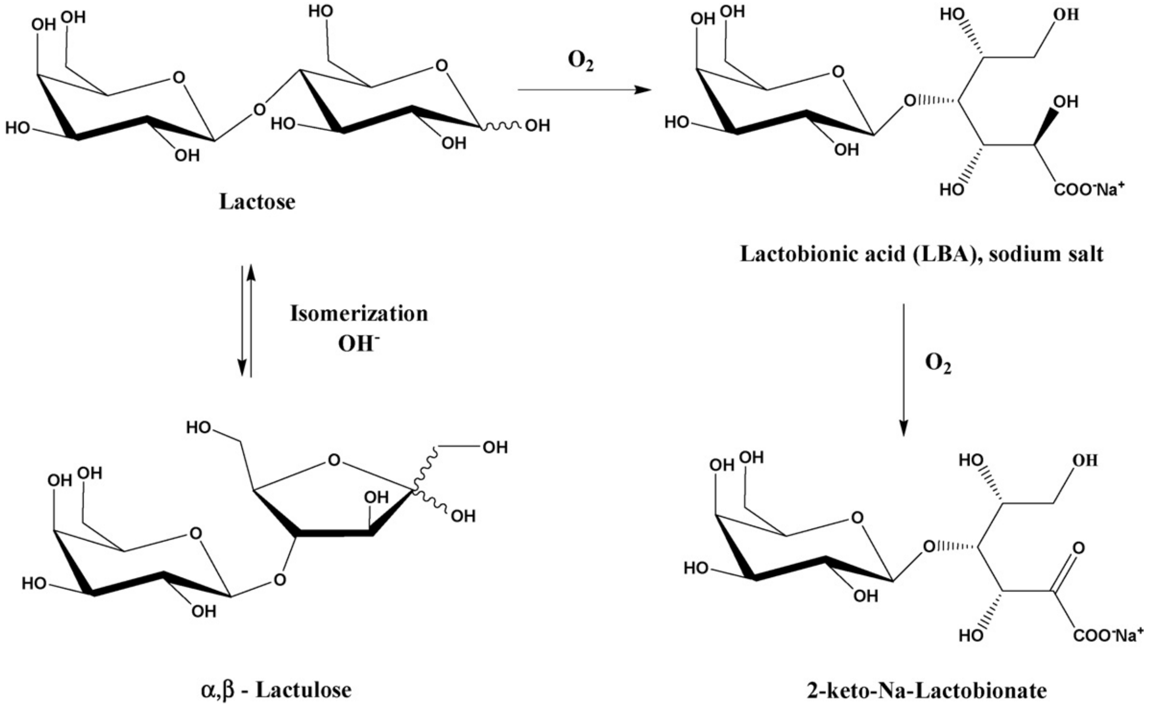

Scheme 1. The lactose oxidation scheme.

Furthermore, it has been noted that attempting to explain the enhanced reactivity of small gold nanocrystals on the basis of size alone neglects the importance of the underlying support [14]. Thus, the support effect has to be addressed in detail while developing gold catalysts, not only the size of the gold nanoparticles. In addition to the size and support effects, also electronic state of the gold particles may be crucial for the activity. Catalyst activity appears to depend strongly on the method of synthesis, the nature of the support, the size of the gold particles and the thermal history of the catalyst.

Previously [15] we demonstrated that gold supported on alumina is 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. It was also found that compared to gold, Pd is more prone to deactivation due to over-oxidation (e.g. oxygen poisoning) of the Pd metal. Both catalysts were deactivated under conditions of high pH and high temperature. In a series of consecutive experiments, gold catalysts demonstrated higher durability than their palladium counterparts [15]. In the present study gold nanoparticles on several supports were used in the oxidation of lactose.

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. Detailed description of the setup can be found in Ref. [1]. The reactor consists of dry and wet compartments which enables the operation of pH and reference electrodes at elevated pressures. A constant gas flow through the reactor was utilized. The gas applied was a mixture of oxygen in nitrogen. The stainless steel reactor walls were utilized as an electrode collector for measurements of the catalyst potential. Potential measurements were performed by means of an Ag/AgCl/3M KCl electrode (Metrohm 6.0733.100). Catalytic experiments were performed in a semi-batch mode. After introducing of the catalyst suspended in water, it was pre-reduced 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). Typically, 2.5 ml/min oxygen flow rate was applied. The pH was kept constant during the experiments by controlled addition of 2.5 M NaOH solution. The majority of experiments were conducted at pH 8. During the reaction the samples of the liquid phase were taken from the reactor and 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 Ref. [16].

2.2. Preparation of catalysts

Gold catalysts Au (2 wt.%)/Al_2O_3, Au (2 wt.%)/SiO_2, Au (2 wt.%)/TiO_2, Au (2 wt.%)/Fe_2O_3, Au (2 wt.%)/Fe_3O_4 and Au (2 wt.%)/ZrO_2 were synthesized by means of a deposition–

precipitation method. The support alumina (Versal VGL-25, <63 μm fraction), SiO_2, (Merck, 40–63 μm fraction), TiO_2 (Degussa Aerolyst 7708, 45–63 μm fraction), Fe_2O_3 (Aldrich, <5 μm, 99%), Fe_3O_4 (Aldrich, <5 μm, 98%) and ZrO_2 (Aldrich, <5 μm fraction, 99%), were precalcined (5 °C/min to 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 (generally 5 g) were prepared and placed on a heating plate with magnetic or mechanical stirring (250 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 in air (10 °C/min to 200 °C, held for 2 h).

As a comparison, Au (0.8 wt.%)/Al_2O_3, Au (1 wt.%)/TiO_2 and Au (1 wt.%)/ZnO by Mintek (South Africa) were tested. These samples were crushed and sieved before catalyst testing. The fraction below 63 μm was used in order to eliminate the influence of internal mass transfer limitations.

2.3. Characterization of catalysts

A Carlo Erba sorptometer 1900 was utilized in the measurement of the surface area and micropore volume by nitrogen physisorpion. BET method was used to calculate the surface areas. Fresh catalyst samples were used in the analysis.

Field emission electron microscopy (FESEM Jeol JSM-6300F) and energy-filtered transmission electron microscopy (EFTEM LEO 912 OMEGA) equipped with an energy dispersive X-ray detector were utilized in the determination of the gold nanocluster sizes.

A Perkin-Elmer 5400 ESCA was used for the XPS analysis with monochromatized Al Kα radiation (1486.6 eV) at 300 W power. In the spectrometer a pass energy setting of 17.90 eV was used. Carbon 1s line at 284.7 eV was used as binding energy (BE) reference. Precision of the binding energy (BE) values is ±0.15 eV. The catalysts were calcined in 200 °C prior to analysis and stored in air. During the analysis, pressure in the analysis chamber was 8×10^{-8} mbar. Charging issues were observed and a flood gun was used to prevent the surface from charging during X-ray bombardment, with the exception of well-conducting carbon supported catalyst. Adventitious carbon 1s line was used as binding energy reference to correct for charging during the analysis.

3. Results and discussions

The prepared gold catalysts were tested in the oxidation of lactose (Table 1). The activities were compared using the time when the conversions 20 and 50%, respectively, were reached, corrected by the metal loading. Table 1 thus displays the values of time (min) needed to reach a certain conversion level multiplied by the amount of gold in the catalyst (g). The concentration curves for the lactose oxidation on catalysts with 2% of gold are shown in Fig. 1.

Obviously, the catalysts display different activity, the most active being Au (2 wt.%)/Al_2O_3. Almost zero order dependence in lactose concentration is observed for it, while for e.g. Au (2 wt.%)/Fe_3O_4 despite substantial initial activity, significant deactivation is visible and the oxidation reaction decelerates after some 20% of conversion is reached.

It was interesting to compare the values of electrochemical catalyst potential for these two catalysts. Time or conversion dependences of the catalyst potential reflect the situation with lactose and oxygen coverage on the surface. Fast increase of catalyst potential indicates saturation of the surface by oxygen. For palladium-based catalysts provided that saturation is fast, the surface is over-oxidized, leading to materials with low activity. According to the catalyst potential measurements, in the case of gold catalysts and contrary to palladium, the surface is saturated by oxygen at rather low conversion levels (Fig. 2). Interestingly enough, for gold supported on Fe_3O_4 this saturation level is approaching very slowly.

Table 1
Catalytic performance of various Au catalysts in lactose oxidation (60 °C, pH 8, oxygen flow rate 2.5 ml/min, $m_{cat} = 0.05$ g)

Entry	Catalyst	$m \times t_{20\%}$ (g_{Au} min)[b]	$m \times t_{50\%}$ (g_{Au} min)[b]	Selectivity to LBA at 20% conversion
1	Au (0.8 wt.%)/Al_2O_3[a]	9.12	27.52	94.3
2	Au (1 wt.%)/TiO_2[a]	7.4	18	95.1
3	Au (1 wt.%)/ZnO[a]	5.6	17.8	93.9
4	Au (2 wt.%)/Al_2O_3	4.5	11.2	95.3
5	Au (2 wt.%)/SiO_2	10.1	n.a.	95.2
6	Au (2 wt.%)/TiO_2	9.6	n.a.	90.4
7	Au (2 wt.%)/Fe_3O_4	9.8	n.a.	90.3
8	Au (2 wt.%)/Fe_2O_3	n.a.	n.a.	n.a.
9	Au (2 wt.%)/ZrO_2	7.1	n.a.	91.2

n.a.: conversion level of either 20 or 50% was not achieved.

[a] 0.2 g of catalyst was used.

[b] *m*: mass of gold in the catalyst sample (g), *t*: time (min) needed to reach 20 or 50% conversion.

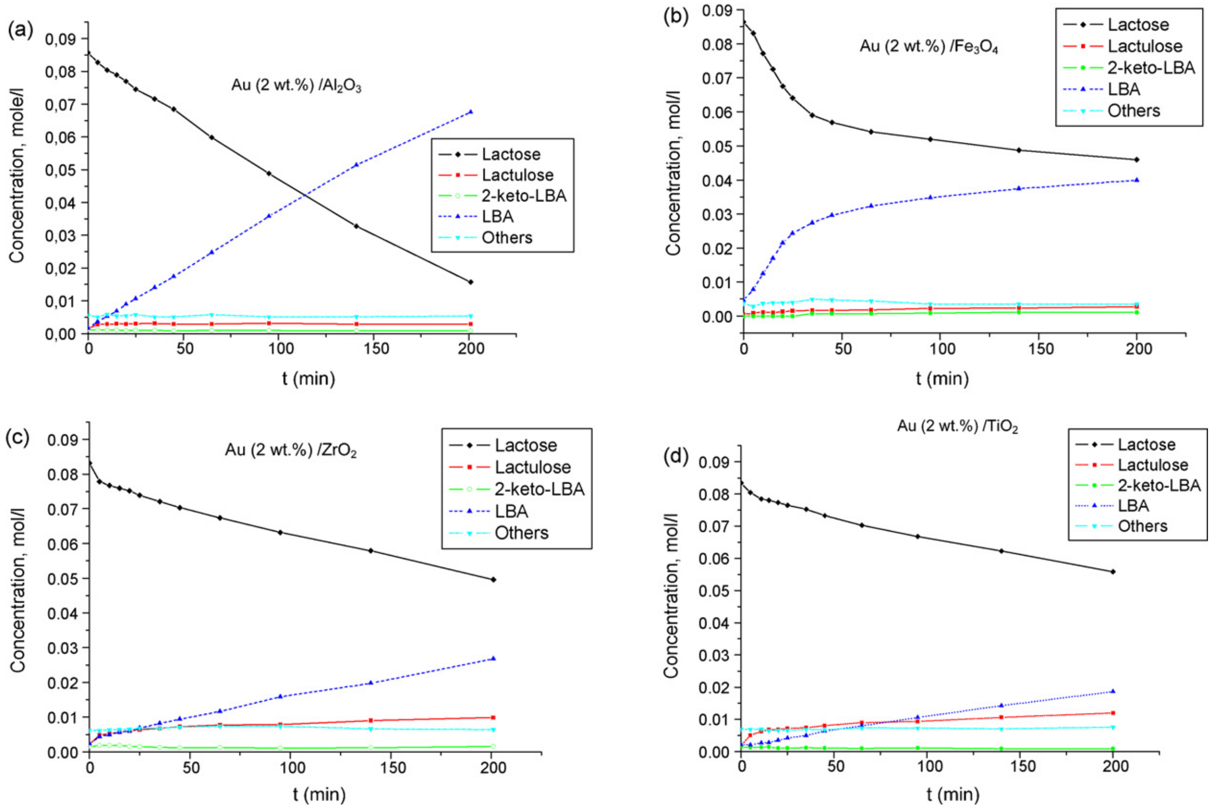

Fig. 1. Lactose oxidation at 60 °C, pH 8, oxygen flow rate 2.5 ml/min, m_{cat} = 0.05 g over (a) Au (2 wt.%)/Al_2O_3, (b) Au (2 wt.%)/Fe_3O_4, (c) Au (2 wt.%)/ZrO_2 and (d) Au (2 wt.%)/TiO_2.

Contrary to Au (2 wt.%)/Fe_3O_4 gold supported on Fe_2O_3 showed much low activity (Table 1). Such low activity of catalysts supported on iron oxides could be at least partially related to the low support surface area, which makes it more prone to deactivation, as there is less possibility for the formed coke to migrate from the metal particles to the support.

In the case of lactose oxidation on Au (2 wt.%)/TiO_2, besides lower reaction rate than for Au (2 wt.%)/Al_2O_3, also somewhat lower selectivity is observed, mainly due to higher lactulose formation. At the same time, for Au (2 wt.%)/TiO_2 the catalyst surface is saturated by oxygen almost in the same way as for Au (2 wt.%)/Al_2O_3 (Fig. 2b).

Experiments with commercial catalysts were conducted with higher catalyst amounts due to lower gold loading (Fig. 3).

Closer comparison between these catalysts reveals that Au (1 wt.%)/TiO_2 was the most active (Fig. 4a), the ratio between lactobionic acid and 2-keto-LBA is practically identical (Fig. 4b), while selectivity to the by-product lactulose over Au (1 wt.%)/TiO_2 is the lowest (Fig. 4c). As expected, the electrochemical catalyst potential followed the behavior,

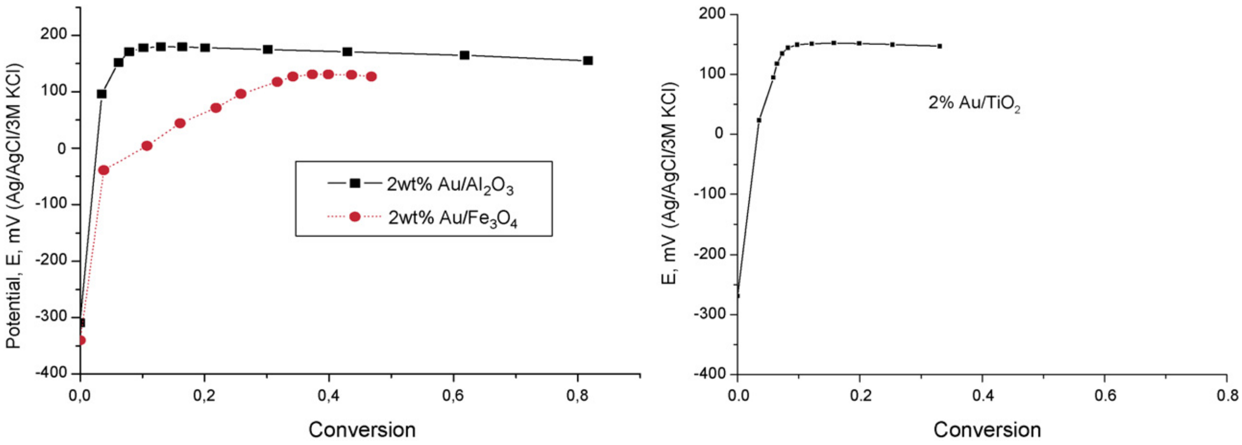

Fig. 2. Electrochemical catalyst potential vs. conversion at 60 °C, pH 8, oxygen flow rate 2.5 ml/min, m_{cat} = 0.05 g over (a) Au (2 wt.%)/Al_2O_3 and Au (2 wt.%)/Fe_3O_4 and (b) Au (2 wt.%)/TiO_2.

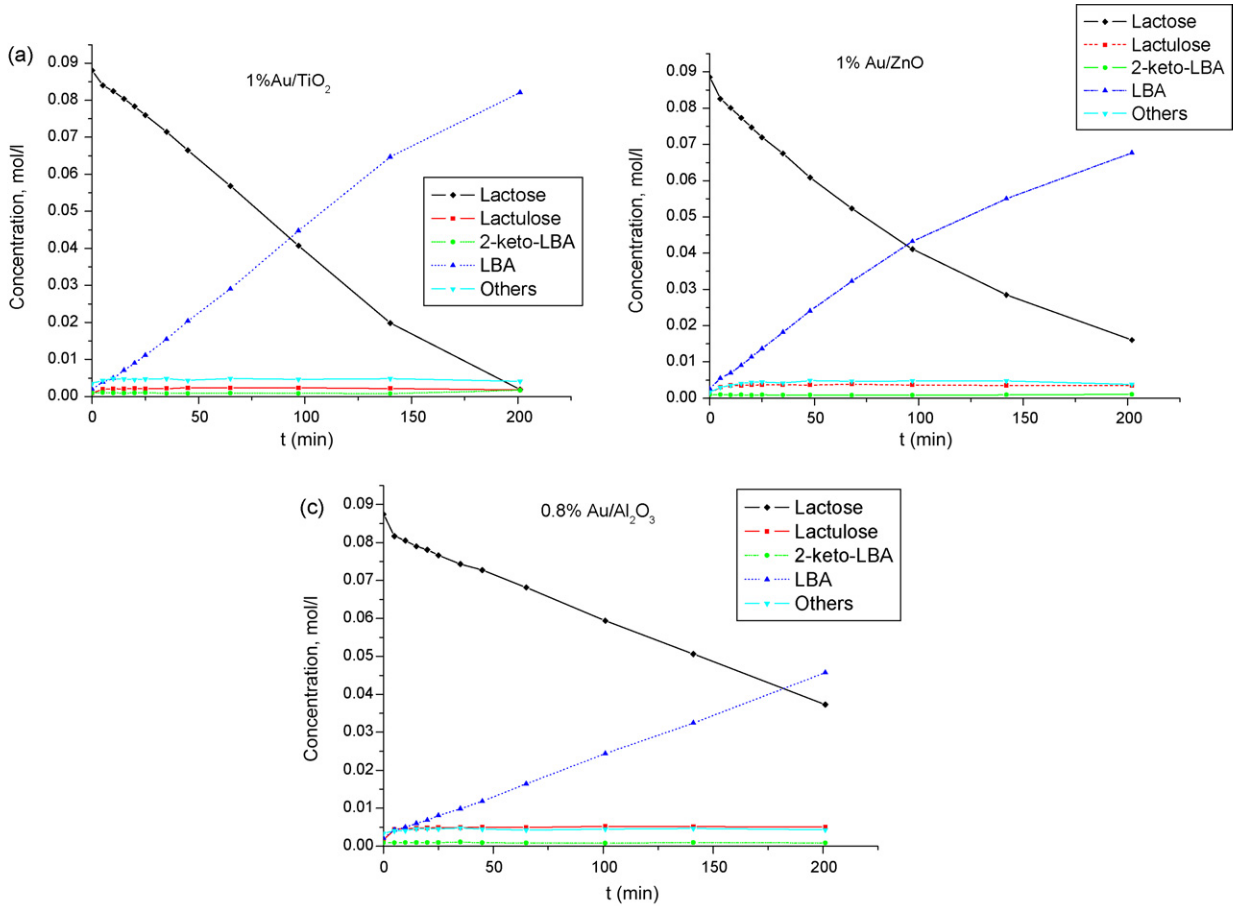

Fig. 3. Lactose oxidation at 60 °C, pH 8, oxygen flow rate 2.5 ml/min, m_{cat} = 0.2 g over (a) Au (1 wt.%)/TiO_2, (b) Au (1 wt.%)/ZnO and (c) Au (0.8 wt.%)/Al_2O_3.

which could be expected for active gold catalysts (Fig. 4d), e.g. a fast increase of potential into the oxidized area was achieved.

Fig. 5 displays a comparison between the catalytic performance of commercial Au (1 wt.%)/TiO_2 and self-prepared Au (2 wt.%)/Al_2O_3 catalysts tested in the present study, showing that the latter catalyst is significantly more active.

A temperature increase to 90 °C, although enhancing initial catalyst activity, resulted in a substantial deactivation at prolonged reaction times, significant formation of lactulose and other by-products and, thus, in a very low selectivity towards the targeted lactobionic acid (Fig. 6).

After an initial increase the electrochemical potential is reaching the oxidized region, corresponding to this temperature, at the conversion level of ca. 25% (Fig. 6b), while at low temperatures it happens already at ca. 10% of conversion (Figs. 2b and 4d). The reason for such behavior in principle could be in lower oxygen solubility at higher temperatures and/or in side reactions, caused by the elevated temperature. Both explanations are feasible, as it was demonstrated previously for palladium [1] and gold [15] catalysts, that with lower oxygen supply the surface is less saturated with oxygen and thus longer time is needed to reach the same level of electrochemical potential if the reaction is conducted at the same temperature.

Table 2
Au clusters size ranges, specific surface area and micropore volumes for tested catalysts

Catalyst	Au cluster size (nm)	BET area (m^2/g)	Micropore volume (cm^3/g)
Au (0.8 wt.%)/Al_2O_3[a]	–	253 (support)	0.67 (support)
Au (1 wt.%)/TiO_2[a]	2.1 ± 0.8	46	0.35
Au (1 wt.%)/ZnO[a]	–	48	0.23
Au (2 wt.%)/Al_2O_3	1–2	368	0.13
Au (2 wt.%)/SiO_2	4–50	155	0.24
Au (2 wt.%)/TiO_2	4–5	44	0.28
Au (2 wt.%)/Fe_3O_4	2–3	5.5	0.002
Au (2 wt.%)/Fe_2O_3	2–3	15	0.07
Au (2 wt.%)/ZrO_2	2–4	7	0.02

[a] Data provided by MINTEK (South Africa).

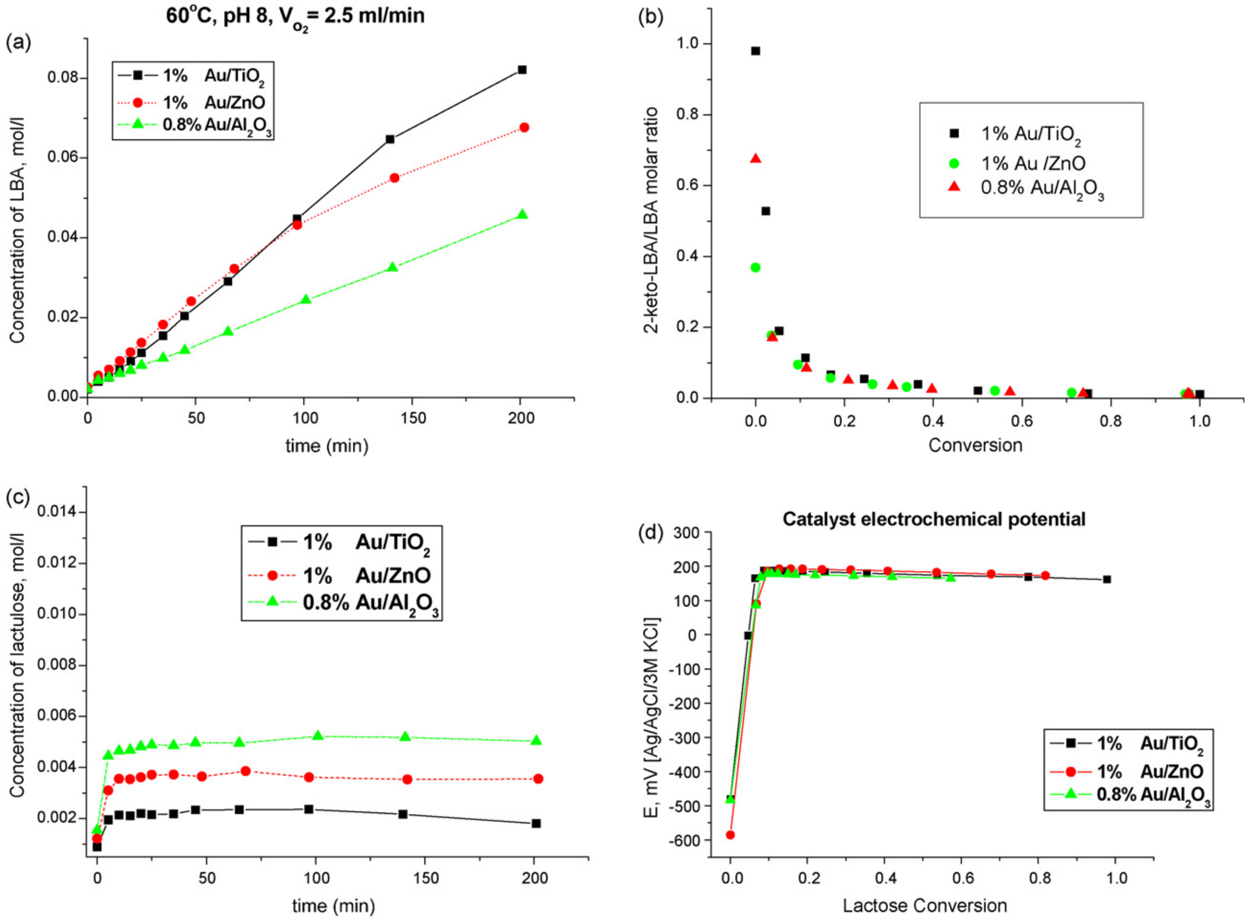

Fig. 4. Lactose oxidation over Au (1 wt.%)/TiO$_2$, Au (1 wt.%)/ZnO, Au (0.8 wt.%)/Al$_2$O$_3$ at 60°C, pH 8, oxygen flow rate 2.5 ml/min, m_{cat} = 0.2 g (a) comparison of LBA formation, (b) 2-keto-LBA/LBA molar ratio, (c) selectivity to lactulose and (d) catalyst electrochemical potential.

When temperature is increased the final level of the electrochemical potential is somewhat lower, as demonstrated for Pd/C [1]. Additionally oxygen accumulation on the surface could be delayed, as oxygen is consumed in side reactions requiring more than stoichiometric amounts of oxygen needed for LBA formation.

Similar detrimental influence of a temperature increase above a certain optimum was reported for oxidation of lactose and maltose over low loaded gold catalysts (ca. 0.5 wt.%) supported on titania and alumina [17]. The direct comparison, however, between the literature results and the present work is not straightforward, since lactose oxidation in Ref. [17] was conducted in a glass reactor of 600 ml with a rather high liquid load (500 ml). This together with a not very efficient magnetic stirring could result in significant influence of mass transfer, somehow compensated by a very high oxygen flow rate (500 ml/min).

Catalyst characterization results of the self-prepared catalysts indicated that Au nanoparticles in the range of few nanometers were formed. The catalyst with the highest activity, i.e. gold on alumina, also had the smallest gold crystals (Table 2). Fig. 7a and b illustrates sample EFTEM images of the gold catalysts. For each sample, a crystalline cubic close-packed Au phase is identified by the diffracting (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) lattice planes. In addition, either diffracted rings or spots with a corresponding lattice spacing of ~3.56 and ~2.93 Å were found for all samples except silica support (this might be the starting Au-compound). Moreover, the alumina and silica support materials seem to be amorphous.

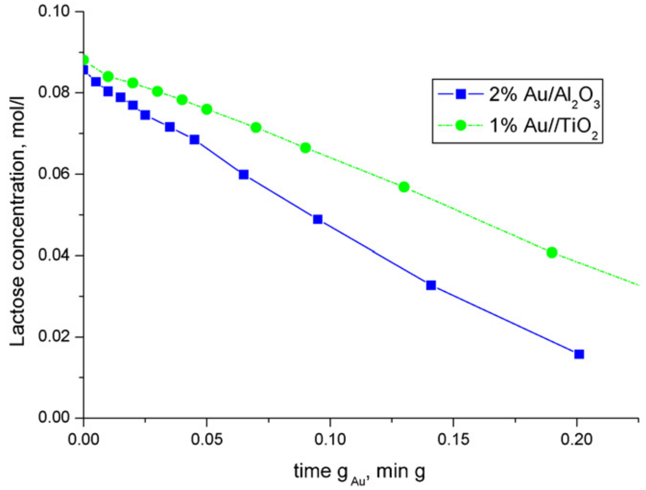

Fig. 5. Oxidation of lactose on Au (1 wt.%)/TiO$_2$ and Au (2 wt.%)/Al$_2$O$_3$ at 60 °C, pH 8 and oxygen flow rate 2.5 ml/min. Concentration vs. gold mass proportional time coordinate.

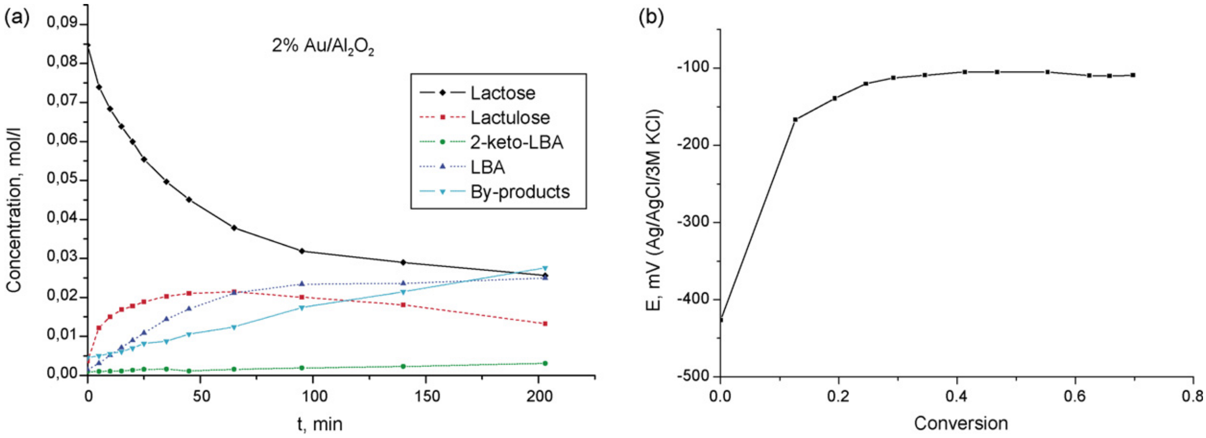

Fig. 6. Lactose oxidation over Au (2 wt.%)/Al_2O_3 at 90 °C, pH 8, oxygen flow rate 2.5 ml/min.

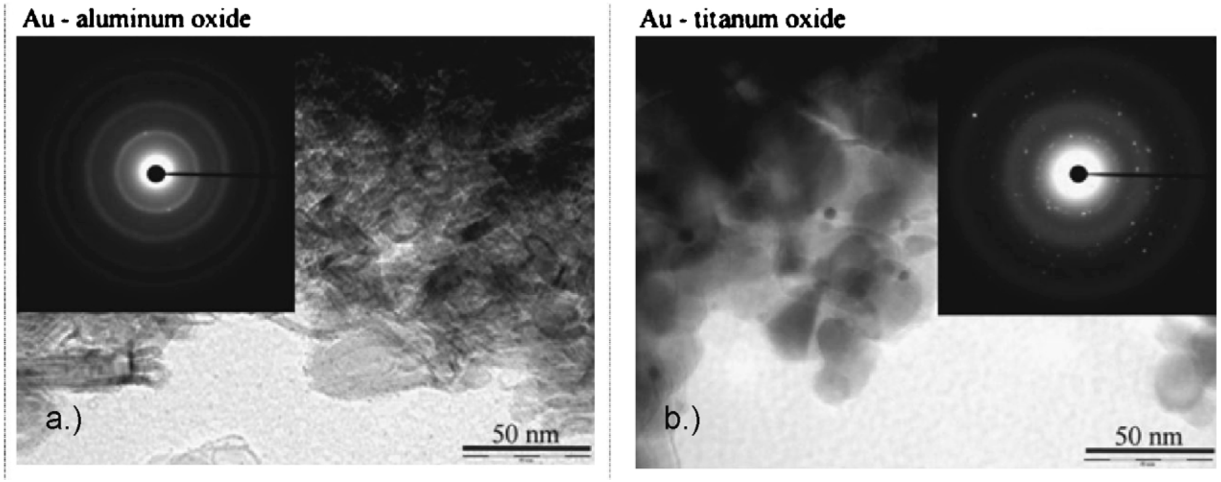

Fig. 7. An EFTEM image coupled to an electron diffractogram of (a) Au (2 wt.%)/Al_2O_3 and (b) Au (2 wt.%)/TiO_2 catalysts.

The Au/Al_2O_3 mixed oxide (Versal) had a clearly higher surface area than any other oxide material. Thus, the resulting gold clusters were likely to be better dispersed onto a larger surface (Table 2). In conclusion, this is one plausible reason for the superior activity of the alumina-supported catalyst.

Au 4f binding energies confirm that no compounds exist with positively charged gold atoms. The noble metal was found to be in Au^0 state (Au $4f_{7/2}$ at 84.1 eV) [18] on alumina-, iron oxide- and zirconia-supported catalysts. In the SiO_2 supported catalyst, charging issues resulted in a broad line with a shift towards lower binding energy despite all the efforts to balance the charging. In Au/Fe_2O_3 and Au/ZrO_2 a weak component (1% of the main peak) with a binding energy of 82.5 eV (as in Au/SiO_2 catalyst) was found in the line fitting procedure and, in Au/TiO_2 catalyst, a low binding energy was found (83.1 eV). They are interpreted as charging effects in Au(0) particles spread over porous support material with no chemical bonding to the support material, therefore the catalysts have a strong tendency toward differential charging during the X-ray bombardment. It can be concluded that gold was in metallic state in all of the tested catalysts. XPS is, however, an *ex situ* method and the results are not conclusive concerning the catalysts performance during the reaction. Hence, the differences in the performance of various catalysts may still be due to their different oxidation state during the reaction.

4. Conclusions

Several supported gold catalysts were successfully applied for lactose oxidation with "*in situ*" monitoring of electrochemical catalyst potential. Very high selectivity to D-lactobionic acid (sodium salt) was achieved at rather mild conditions, e.g. 60 °C and pH 8. While high selectivity seems to be an intrinsic feature of several gold catalysts, the activity was evidently dependent on the nature of the support.

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