# Immobilised synzyme-like gold nanoparticles for the oxidation of sugars to sugar acids

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## Introduction

The catalytic oxidation of the low-molecular carbohydrates as renewable resources (e.g. glucose, maltose and lactose) is useful both from the ecological and economical point of view as the products, i.e. the corresponding sugar acids (Fig. 1), have various applications in life sciences (food, pharmaceuticals, cosmetics) and as biodegradable complexing agents in detergents.

Nowadays, sugar acids are produced by biotechnological processes, i.e. fermentation, involving *gluconobacter suboxydans* and *aspergillus niger*. The fermentation process is established only for the production of gluconic acid from glucose (annual production amount 100 000 tons) and to a much lesser extent for the production of lactobionic acid from lactose. Unfortunately, fermentation processes for the production of other sugar acids are not sophisticated so that the availability of sugar acids in industrial quantities so far is limited to gluconic and lactobionic acid despite the potential broad application range of sugar acids in general.
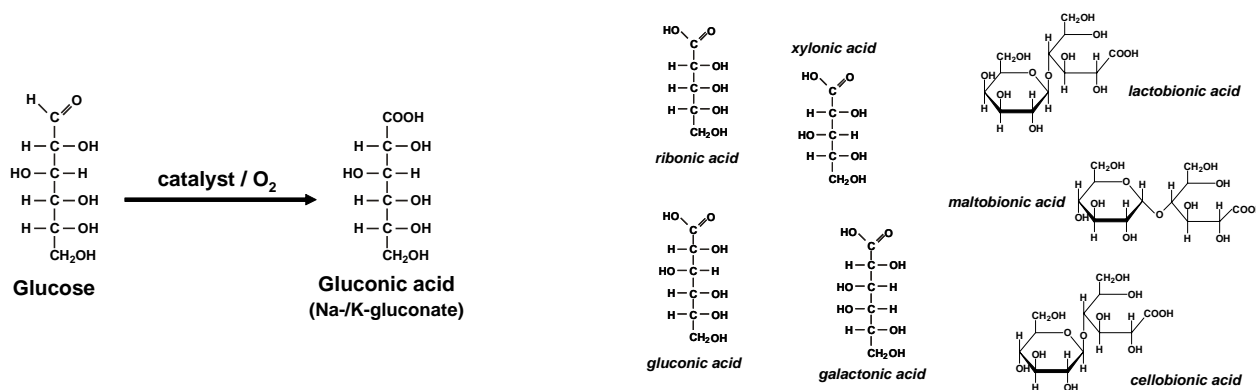


**Figure 1: Left: Reaction scheme of the catalytic oxidation of glucose to gluconic acid/gluconate; right: Structure of various interesting sugar acids available by gold-catalyzed oxidation.**

Sugar acids may also be produced by chemical oxidation, especially using heterogeneous metal catalysts. Although manifold efforts have been undertaken within the last 60 years to establish such a metal-catalyzed oxidation process the low activity, selectivity and long-term stability of the applied platinum- and palladium-based catalysts so far prevented an industrial application. Very recently, gold nanoparticles have been used for this reaction (Biella 2002, Comotti 2006, Baatz 2007 a & b, Mirescu 2007 a & b, Thielecke et al. 2007 a & b). Due to their outstanding properties gold nanoparticles may in the future replace the fermentation processes for the industrial production of sugar acids.

## Material and methods

The procedure of the formation of gold nanoparticles on alumina includes the immobilization of an ionic gold precursor (HAuCl$_4$ or derivatives thereof) on the alumina by adsorption and a successive calcination process or reduction process, the latter either in gas-phase with hydrogen or in the liquid

phase by sodium borohydride. Gold nanoparticles have been immobilized on both alumina powders and alumina beads (Fig. 2). Alumina beads were prepared via the sol-gel method from boehmite powders with the JetCutter technology. Details about the preparation procedures, which are crucial for the generation of the gold nanoparticle structures, can be taken from (Baatz 2007 a & b, Mirescu 2007 a & b).
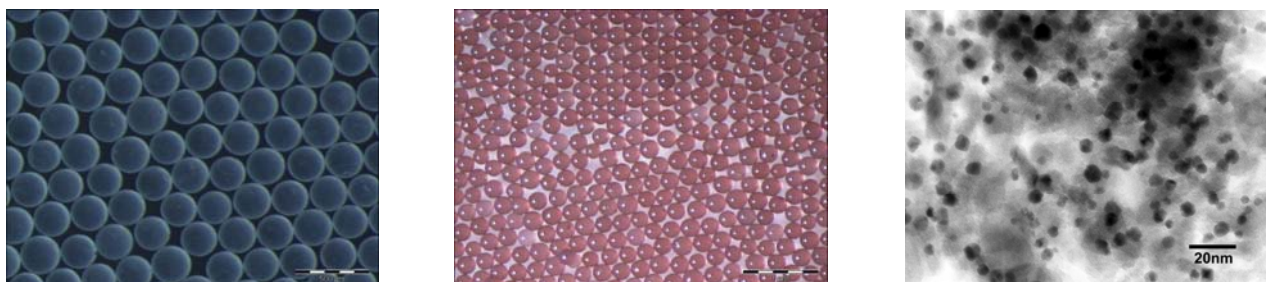


**Figure 2: Left: Alumina beads (Ø = 250 μm) prepared by the sol-gel method with the JetCutter technology; middle: 0.3 % gold nanoparticles immobilized on alumina beads; right: TEM micrograph of gold nanoparticles immobilized on alumina.**

Immobilized gold nanoparticles were used for the liquid-phase oxidation of various sugars to their corresponding sugar acids. Reactions were carried out in aqueous-phase at mild reaction conditions (usually pH 9, 40 °C). Oxygen has been used as oxidizing agent at 1 bar partial pressure unless otherwise stated. Both batch and continuous-flow conditions have been applied. Initial carbohydrate concentrations ranged from 0.2 – 57.5 weight% (wt%). Typically, a molar ratio between carbohydrate and gold of 20000 has been used. Due to the slight alkaline pH value, which was maintained by titration with NaOH, not the corresponding sugar acids but their sodium salts have been produced.

**Results and Discussion**

Gold nanoparticles have been used for the oxidation of various carbohydrates. Whereas ketoses, such as fructose, sucrose or palatinose, were not oxidized at all, aldoses, such as ribose, xylose, glucose, galactose, maltose, lactose or cellobiose, were oxidized at the aldehyde function at C1 to the carboxylate, i.e. to the salt of the corresponding aldonic acid (e.g. glucose $\rightarrow$ gluconate). The aldonic acids were formed with a total selectivity, i.e. no by-products were detected (Fig. 3).
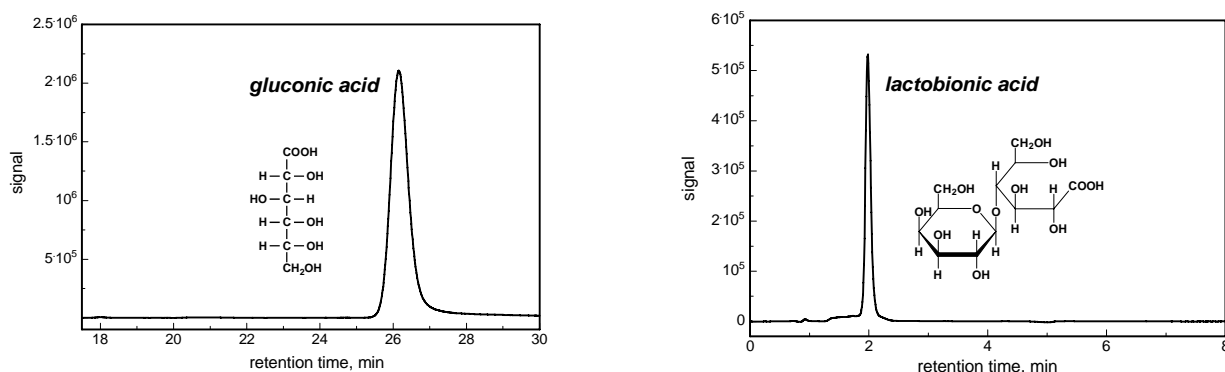


**Figure 3: Chromatograms of the reaction solution after complete glucose or lactose conversion with an Au/Al$_2$O$_3$ catalyst. The selectivity for gluconic acid (left) and lactobionic acid (right), respectively, is > 99.5 %.**

Thus, gold nanoparticles exhibit not only a pronounced substrate selectivity but also a total product selectivity. Such high specificity is known for enzymes but is not at all common for heterogeneous catalysts so that these gold nanoparticles can be regarded as synthetic enzymes, i.e. synzymes. In contrast to biocatalysts, the gold synzymes can easily be used under different reaction conditions, e.g. substrate concentration, pH values, oxygen pressures or temperatures, without loosing their selectivity. A high oxygen partial pressure and industrial relevant glucose concentrations (20 – 30 wt%) are favorable conditions for the gold synzymes (Fig. 4). However, they can also be used to convert highly concentrated glucose solutions up to the solubility limit. The complete conversion of a 57.5 wt% glucose solution results in a ready-to-sale 50 wt% gluconate solution. No purification or any other process step despite catalyst separation by filtration is needed in this case.

In the industrially established fermentation process for the production of sodium gluconate maximum space-time yields of 13 g $L^{-1}$ $h^{-1}$ are reported (Roehr et al. 1996). Without being optimized in this regard gold synzymes exhibit space-time yields of more than 200 g $L^{-1}$ $h^{-1}$.
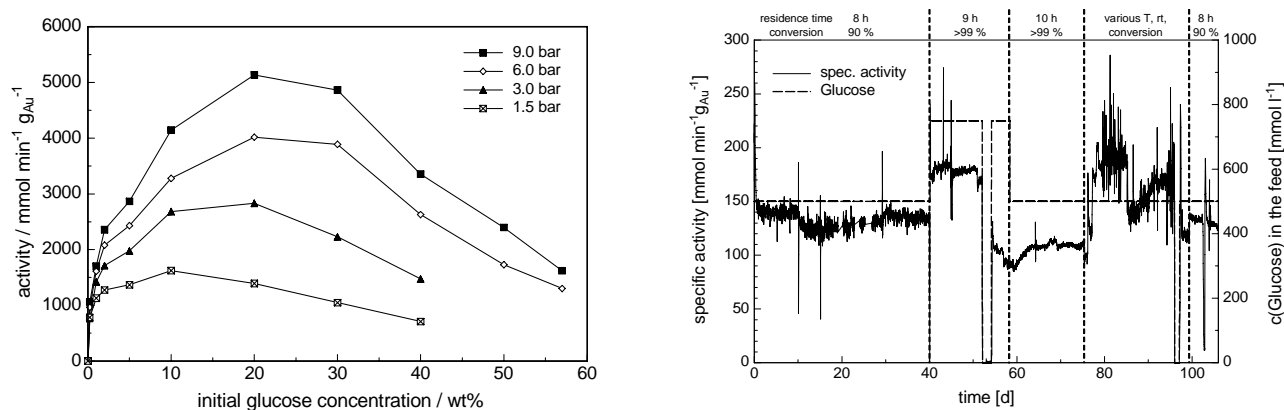


**Figure 4: Left: Catalyst activity vs. initial glucose concentration for batch glucose oxidation at different oxygen partial pressures; right: Long-term stability of a 0.3 % Au/Al$_2$O$_3$ catalyst in continuous-flow glucose oxidation at different reaction conditions.**

The long-term stability of any kind of catalyst, biocatalyst or chemical catalyst, is one of the most crucial points for an industrial production process. For different gold synzymes their long-term stability has been evaluated both in repeated batch experiments and under continuous-flow conditions.

In Fig. 4 the activity of a gold synzyme is displayed for a continuous-flow experiment which has been carried out in a continuous stirred-tank reactor (CSTR) for 110 days. During this period reactions conditions such as glucose feed concentration, residence time, conversion, and temperature have been varied. During this experiment several failures occurred, such as oxygen supply blackout (day 10), interruption of NaOH dosage leading to a pH value of less than 7 (day 19) and electrical power blackouts (days 23 and 26). No matter which failure occurred the synzyme activity was restored immediately after the failure has been corrected.

More severe problems derived from microbial contaminations at days 54, 96 and 109 which required an *in-situ* disinfection procedure in order not to terminate the experiment. Therefore, both the reactor system and the gold synzyme inside the reactor have been regenerated *in-situ* either by disinfection with isopropanol (days 55-57) or by heating up the whole system to 70 °C (days 75 - 76). Microbial re-contamination was more effectively prevented by isopropanol treatment (no contamination within the next 42 days) than by heat treatment (recontamination after 13 days). Even those *in-situ* regeneration procedures didn't affect the activity or the selectivity of the synzyme; its activity remained constant at equal reaction conditions, e.g. from day 1 – 40 and from day 99 – 110 (Fig. 4). Hence, the gold synzyme is very robust, resists changing reaction conditions

and can thus be regarded as extremely long-term stable and, therefore, as suitable for industrial application.

During the continuous-flow experiment shown in Fig. 4 about 4 tons of gluconate have been produced per gram gold. Although gold is a rather expensive metal, the gold costs sum up to only less than 0.3 €Cent per kilogram produced gluconate for this 110 day run.

## Conclusions

Gold nanoparticles immobilized on alumina were used for the oxidation of carbohydrates to their corresponding sugar acids. This process offers a new and versatile method for the production of various sugar acids with a so far unknown high selectivity, long-term stability and space-time yield. Compared to the industrial fermentation process these new gold synzymes perform much better. This new technology is currently further exploited in pilot-scale tests.

## References

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