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Selective oxidation of carbohydrates with gold catalysts: Continuous-flow reactor system for glucose oxidation

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Abstract

For the first time, a continuous-flow liquid-phase oxidation using a gold catalyst is described. A 0.25% Au/Al_2O_3 catalyst was investigated in the continuous-flow carbohydrate oxidation using glucose as the model compound. To achieve this, a continuous stirred tank reactor (CSTR) system was developed in which the powdered catalyst was separated by a combination of an ultrasonic separator and a separation vessel. The continuous-flow glucose oxidation was carried out at 40 °C, pH 9 and 1 bar oxygen partial pressure and maintained for 70 days. During this run-time the residence time and glucose concentration were varied. The alumina-supported gold catalyst showed very high activity and selectivity to gluconic acid. The long-term stability of the gold catalyst was excellent as no loss in activity or selectivity occurred during 70 days of continuous operation.

Keywords: Gold catalyst; Au; Glucose oxidation; Continuous stirred tank reactor; Liquid-phase; Gluconic acid

1. Introduction

Carbohydrates are a promising renewable feedstock as they already possess a stereogenic framework for the synthesis of various organic structures. The catalytic oxidation of sugars is one possibility to use this feedstock by converting it to technologically valuable sugar acids. For example, the biodegradable gluconic acid is used as complexing or acidifying agent in both the food and pharmaceutical industries and is also applied in paper and concrete production. Currently, about 100,000 tonnes of gluconic acid are produced annually almost exclusively with biotechnological processes involving *Aspergillus niger* and *Gluconobacter suboxidans*.

Apart from the biotechnological processes, chemical catalysis can also be used for the oxidation of carbohydrates. First experiments were carried out with a platinum catalyst as early as 1861 [1]. In the 1960s, the platinum catalysed carbohydrate oxidation was studied more systematically, and a reactivity order of the carbohydrates' functional groups was discovered [2]. However, the platinum catalysts used in these studies exhibited rather poor activity and selectivity. Later publications described the promotion of heterogeneous platinum and palladium catalysts with metals like Bi or Pb [3,4], which enhanced the selectivity and activity in glucose oxidation. Unfortunately, these catalysts showed no sufficient long-term stability and a leaching of the second metal has been described [5]. In 2002, Biella et al. [6] reported that carbon supported gold colloids are much more active in glucose oxidation and most notably 100% selective towards gluconic acid. Again, these catalysts showed only an insufficient long-term stability as their activity decreased to only 50% after four runs.

More recent investigations of metal oxide supported gold catalysts showed that such catalysts have excellent properties in the liquid-phase carbohydrate oxidation [7–10]. They have been used for the oxidation of various pentoses (e.g., arabinose, ribose, xylose, lyxose), hexoses (e.g., glucose, mannose, rhamnose, galactose, *N*-acetyl-glucosamine) and di-/oligosaccharides (e.g., lactose, cellobiose, melibiose, maltotriose). In these reactions, the gold catalysts showed a very high activity and a total selectivity to the corresponding aldonic acids. Furthermore, these gold catalysts showed no loss of activity in several repeated batches [7,9].

The aim of this study was to check the long-term stability of such metal oxide supported gold catalysts for the oxidation of carbohydrates under continuous-flow conditions. A continuous stirred tank reactor (CSTR) system was designed to enable the continuous mode, allowing the separation of a powdered catalyst with an ultrasonic separator. Glucose was chosen as a

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model compound to test an alumina-supported gold catalyst in this liquid-phase carbohydrate oxidation reaction.

2. Experimental

2.1. Reactor design

A scheme of the reactor system is shown in Fig. 1. The CSTR comprises a thermostatted glass reactor (volume 1000 ml) equipped with temperature sensor, pH electrode, burette, glass frit for oxygen supply, filling-level electrodes, feed tube and suction tube for the efflux. The liquid level is kept constant at 750 ml by a filling-level meter, which controls a pump (Electronic E2001, Prominent, Germany) to fill substrate (glucose solution) into the reactor. The pH is kept constant with a pH unit (Dulcometer PHD, Prominent, Germany). The titration solution is 16 wt% NaOH (Roth, Germany). The NaOH consumption is measured by a scale and charted every five minutes by a PC. The reaction suspension is stirred at 620 rpm with a horseshoe mixer. The reaction mixture is continuously pumped out of the reactor by a peristaltic pump (ecoline, Ismatech, Switzerland) via the separation system consisting of an ultrasonic separator (BioSep, Applikon, Germany) and an additional separation vessel (500 ml separating funnel) into the efflux reservoir.

The catalyst separation occurs mainly in the ultrasonic separator. This device was primarily developed for the separation of cells in fermentations. It utilizes megahertz range ultrasonic waves to separate suspended solids from the liquid-phase. The separation takes place within a defined volume, the resonator. The resonator is composed of two opposed parallel glass surfaces, of which one surface is piezoelectrically activated and acts as an ultrasonic source. At specifically selected frequencies, a highly frequent acoustic standing field is established within the suspension between the glass walls. The acoustic energy mesh acts as a virtual filter capable of capturing solids within the antinodes of the field. The loose catalyst aggregates formed inside the resonator chamber are continuously pumped back into the reactor by a peristaltic pump (Masterflex console drive, Cole-Parmer Instruments Company, USA). Fig. 2 shows a picture of the working resonator in which the catalyst aggregates appear as small ''vertical lines'' arranged in several horizontal lines from the bottom to the top of the resonator.

Preliminary separation tests were carried out to find optimum separation conditions. Therefore a flow rate of 400 ml h^{-1}, which is equal to the highest flow rate applied during the catalytic tests, was adjusted. The best separation was obtained with 7 W power, 15 min run-time and 3 s stop-time. As the ultrasound field has to be switched-off for at least 3 s every 15 min to be re-established, a small amount of the catalyst is discharged during that time. With the optimized settings the discharge of catalyst particles was only 11.6 mg h^{-1} for 1 g total catalyst amount inside the reactor, which is equal to 99% separation. Despite this very high separation rate, at a catalyst concentration of 2 g l^{-1} the whole catalyst would be discharged after approximately 130 h. Hence, to assure a complete catalyst separation and, thus, long-term continuous conditions, the efflux is pumped into an additional separation vessel. The catalyst particles discharged from the ultrasonic separator sediment there and are pumped back into the reactor once every hour by a diaphragm pump (Electronic E2001). With this method a 100% catalyst separation was achieved during the continuous mode, although approximately 10 % of the catalyst is permanently located in the separation system.

Due to the dosage of glucose and NaOH solution, and the back pumping of the sedimented catalyst, the liquid level of 750 ml varies approximately within a 2% range. As the reactants and the separation vessel are not thermostatted, the temperature inside the reactor varies within a range of 1 K as well.

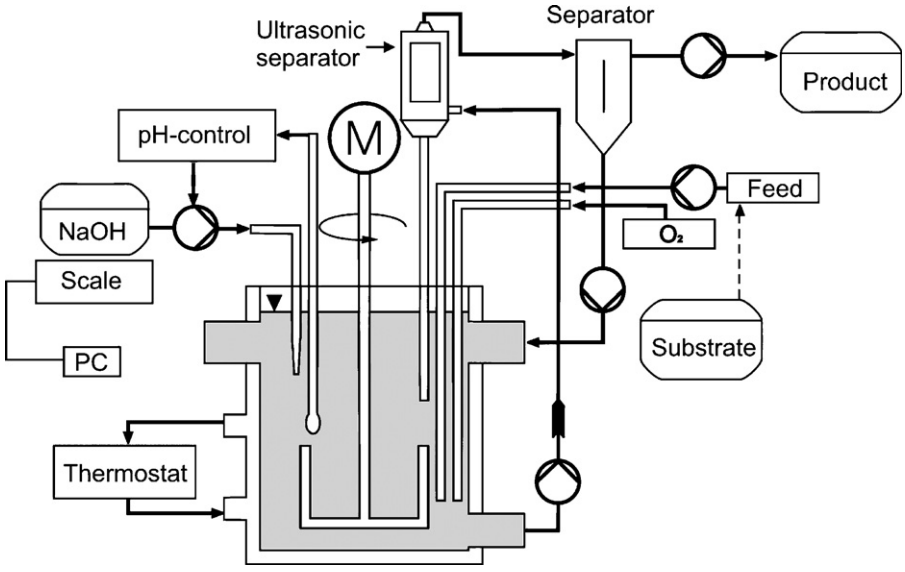

Fig. 1. Scheme of the CSTR for the catalytic oxidation of glucose.

Fig. 2. Photo of the working ultrasonic resonator.

2.2. Residence time distribution

The residence time distribution (RTD) is determined experimentally for the CSTR with conductivity measurements for 750 ml volume under isothermal conditions (40 °C). Two diaphragm pumps (Electronic E2001) establish the feeding and removal of deionised water from the CSTR. The flow rate was obtained by calibration of the pump speeds to ensure the desired feed and efflux rates, as well as a constant residence time. The flow rate was set at 500 ml h^{-1}, which is equal to a residence time of 90 min. The tracer, 2 ml NaOH solution (16 wt%), was injected directly into the CSTR. The conductivity cell was positioned in the efflux to chart the change of conductivity over time. Hence, the $E(t)$-function (RTD) was determined as it is shown in Fig. 3 together with the theoretical CSTR $E(t)$-curve. The x-axis is the non-dimensional time, which is the ratio between the time t and the residence time τ. As the experimental and theoretical functions show very similar characteristics, only negligible dead zones and by-pass flows are present. The residence time derived from the determined $E(t)$-curve was 88 min, which is in good consistence with the adjusted residence time of 90 min. The reactor system is adopted as ideal due to its negligible deviation from the theoretical system.

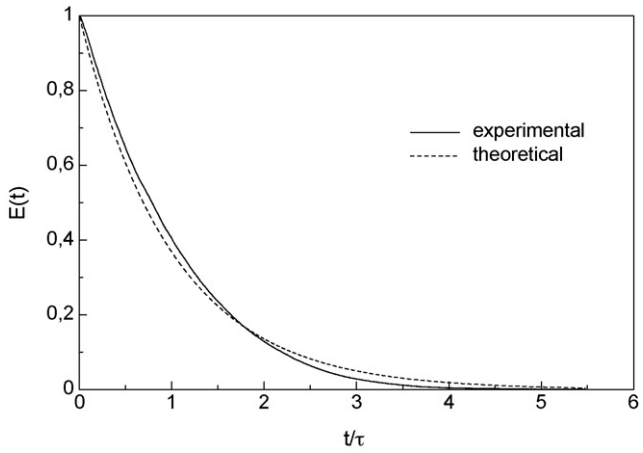

Fig. 3. Retention time distribution of the CSTR system, theoretical and experimental $E(t)$-function.

2.3. Catalyst preparation

Prior to the preparation the alumina support (SCFa-90, Sasol Germany) was sieved. The fraction with the particle diameter of 25–63 μm has been chosen for the catalyst preparation in order to facilitate its separation by the ultrasonic separator under continuous-flow conditions.

The gold catalyst is prepared by the deposition precipitation (DP) method using urea as precipitation agent. Therefore, 10 g of the alumina, 300 ml aqueous solution of urea (0.21 mol l^{-1}) and 5 ml aqueous solution of $HAuCl_4$ (gold content 5 g l^{-1}, Chempur, Germany) are suspended in a thermostatted reactor at 80 °C. The suspension is vigorously stirred for 20 h and cooled to room temperature afterwards. Subsequently, the precursor is filtered and washed over a 25 μm sieve, so that particles smaller than 25 μm are removed which might have emerged through abrasion during the preparation. Afterwards, the precursor is dried overnight at 80 °C and activated by reduction in a hydrogen/nitrogen gas stream (2 l min^{-1}, 10% H_2) at 220 °C for 2 h. The gold content of the final catalyst is equal to 0.25 wt%.

2.4. Continuous-flow glucose oxidation

The continuous-flow glucose oxidation is carried out at 40 °C at a gold catalyst concentration of 2 g l^{-1}. Oxygen is supplied through a glass frit with a flow rate of 500 ml min^{-1} at atmospheric pressure and the pH is kept constant at 9 by adding NaOH solution. Accordingly, sodium gluconate, instead of gluconic acid, is the product of glucose oxidation at this slightly alkaline pH.

The whole continuous-flow experiment was maintained for 70 days and is divided into different sections which differ in retention time (RT) and glucose feed concentration. The glucose feed concentration (D-glucose, Merck, Germany) was varied between 250 and 1500 mmol l^{-1} and the residence time was set between 2 and 8 h. The settings of the whole experiment

Table 1
Summary of the adjusted reaction conditions and the resulting glucose conversion, specific activity and glucose efflux concentration during the continuous-flow glucose oxidation with a 0.25% Au/Al_2O_3 catalyst, RT: residence time

Section	Time (*d*)	RT (h)	*c*(Glucose) feed (mmol l^{-1})	Conversion (%)	Spec. activity (mmol g_{Au}^{-1} min^{-1})	*c*(Glucose) efflux (mmol l^{-1})
1	1–5	2	250	n.s.	n.s.	n.s.
2	5–10	4	250	71	167	73
3	10–12	2	250	55	238	113
4	12–14	2	1500	n.s.	n.s.	n.s.
5	14–18	4	250	80	189	50
6	18–22	4	500	52	245	240
7	22–26	8	500	96	193	20
8	26–39	8	1000	n.s.	n.s.	n.s.
9	39–51	4	250	82	194	45
10	51–70	8	500	91	179	45

can be taken from Table 1, in which also the average values of conversion, specific activity and glucose efflux concentration of each section are shown. If no constant value was reached during one section, it is named ''not specified'' (n.s.). The specific activity describes the formation of sodium gluconate per minute and mass of gold. The concentrations of glucose, sodium gluconate and potential by-products in the feed and efflux were periodically controlled by HPLC (Luna Amino 5 μ column, Phenomenex, Germany). As the selectivity to gluconate was higher than 99.5% during the whole experiment, conversion and specific activity could be calculated directly from the consumption of NaOH. The conversion calculated from the NaOH consumption is in good consistence with the conversion determined by HPLC analysis as only slight variances between 1.5 and 5% were observed.

3. Results and discussion

In contrast to immobilized gold sols [6], alumina- and titania-supported gold catalysts [7] showed excellent long-term stability in catalytic glucose oxidation during several repeated batches. Hence, the described reactor system was applied for continuous-flow glucose oxidation with 1.5 g of an alumina-supported gold catalyst prepared by DP urea with 0.25% gold content. This amount is equal to a catalyst concentration of 2 g l^{-1} and a gold concentration of 5 mg l^{-1} in the reactor.

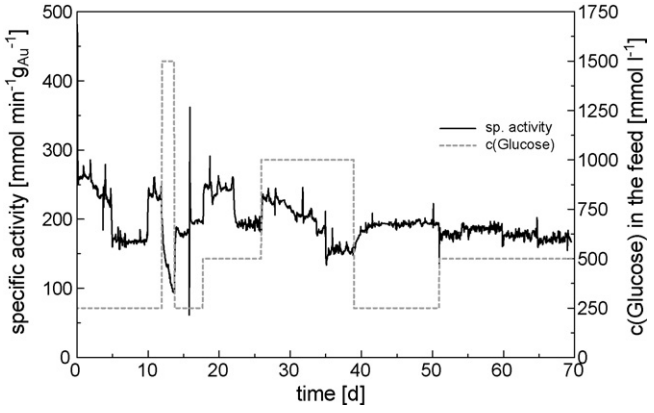

Fig. 4. Specific activity of the 0.25% Au/Al_2O_3 catalyst and applied glucose feed concentration during continuous-flow glucose oxidation.

The continuous-flow glucose oxidation was maintained for 70 d. The specific activity during this run-time is shown in Fig. 4, in which the glucose feed concentration is also mapped. As the figured activity data result directly from the measured NaOH consumption, the curve is not smooth. The ''noise'' is caused by temperature and volume fluctuations as described above. Peaks occur, when settings, the pH-electrode or pump hoses have been changed.

To simplify the description of the whole 70-day experiment, it is divided into sections depending on the settings as shown in Fig. 5. The reaction was started with 250 mmol l^{-1} glucose feed concentration and a residence time of 2 h. During these first 5 days, the specific activity seems to decrease slightly. This activity decrease is apparent and is caused by the fact that some catalyst material is discharged from the reactor into the separation systems during that time. After about 5 days the system reached a steady state. In the next 5 days (Section 2), a stable specific activity and conversion was observed when the residence time was set to 4 h. This was the case in Section 3 as well, when the settings of Section 1 were readjusted for 2 more days. It is noteworthy that only a very short time of approximately 60 min was required to reach a new steady state after the settings, e.g., glucose feed concentration or residence time, were changed.

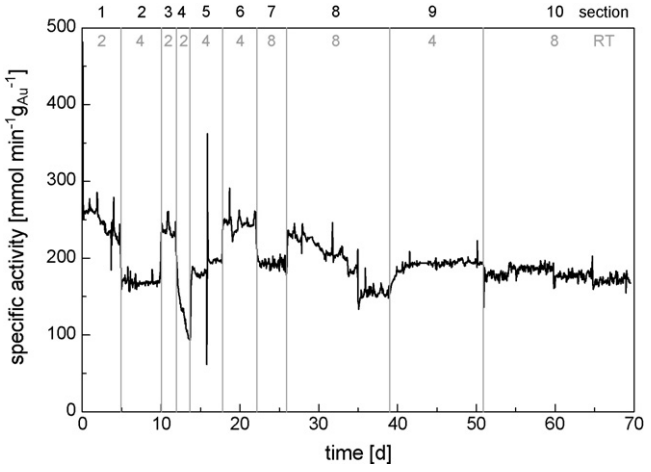

Fig. 5. Sections and adjusted residence time during continuous-flow glucose oxidation, for comparison the specific activity is also mapped as in Fig. 4.

A high product concentration is desirable for technical applications. Here the settings were varied during the run-time to check the influence of glucose feed concentration and residence time on the specific activity and conversion. High glucose feed concentrations were adjusted twice, in Sections 4 and 8. As can be seen in Fig. 4, a considerable decrease in activity was observed in both sections. At a constant retention time of 2 h, for example, an increase of glucose feed concentration from 250 mmol l^{-1} in Section 3 to 1500 mmol l^{-1} in Section 4 leads to an activity decrease of about 60%. This activity drop could either be caused by a kinetic effect or by a deactivation phenomenon. If the activity drop had been caused by a kinetic effect, a steady state should have been reached, which was not observed. Instead, a constant decrease of activity and conversion was noticed. Therefore, a deactivation is more probable, which might be caused by a catalyst fouling with impurities in the glucose charge. The hypothesis of a deactivation phenomenon is supported by the fact that the same deactivation occurs in an alleviated way when the glucose concentration is set to 1000 mmol l^{-1} (Section 8). So far, these results are preliminary, but further studies concerning this deactivation are currently under investigation and will be described in a subsequent paper.

During the 70 days run-time, some settings were repeated to check not only the long-term stability of the catalyst under identical conditions but also whether the specific activity and conversion could be restored after a deactivation occurred. The sections with identical settings over the runtime are shown in Figs. 6 and 7. Fig. 6 shows a constant specific activity in the sections with a glucose feed concentration of 250 mmol l^{-1} and a residence time of 4 h in three different periods. Similarly, a constant specific activity can be noticed in the two sections shown in Fig. 7, when the glucose concentration was 500 mmol l^{-1} and the residence time was set to 8 h. In between the periods displayed in both Figs. 6 and 7, catalyst deactivation due to high glucose feed concentrations occurred. If the catalysts' deactivation were at least partially irreversible, the activity course would not be constant as shown in Figs. 6 and 7. That means that the catalyst deactivation by fouling is reversible, as

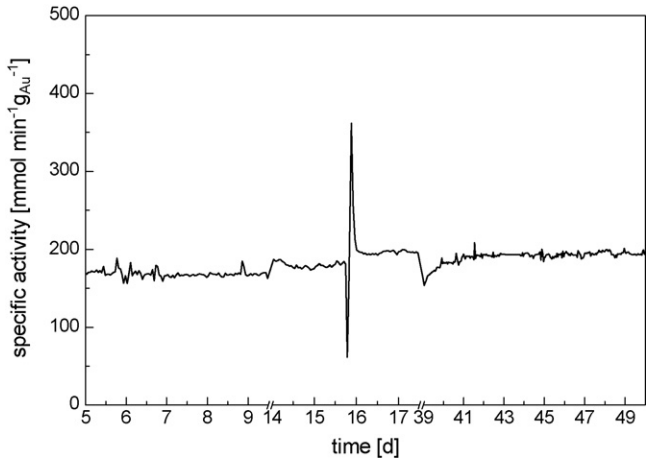

Fig. 6. Specific activity of the 0.25% Au/Al_2O_3 catalyst during the Sections 2, 5 and 9 at a glucose feed concentration of 250 mmol l^{-1} and a retention time of 4 h.

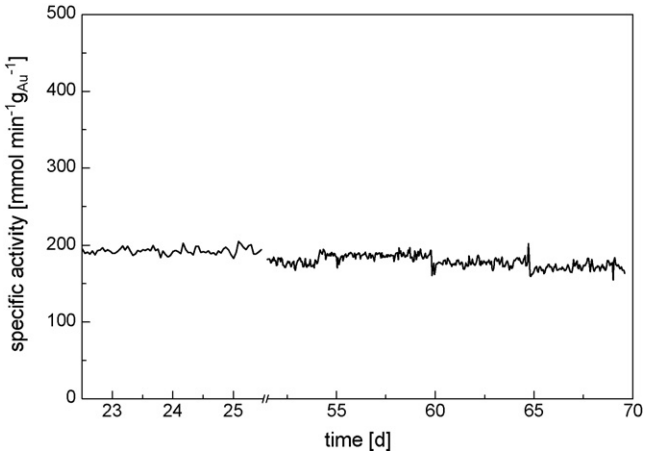

Fig. 7. Specific activity during the Sections 7 and 10 at a glucose feed concentration of 500 mmol l^{-1} and a retention time of 8 h.

the catalyst always fully regenerates when the glucose concentration is lowered again. Obviously, this gold catalyst is not only stable over the long-term but also quite robust.

During the experiment some combinations of residence time and glucose feed concentration lead to similar throughput amounts of glucose, i.e., the same amount of glucose was fed into the reactor each time. Approximately, the same amount of glucose is converted at high glucose throughputs. For example, a high glucose throughput of 94 mmol h^{-1} has been adjusted in Sections 3 and 6. Approximately, 50 mmol h^{-1} glucose are converted in both sections, which means that the glucose concentration inside the reactor (113 and 240 mmol l^{-1}, respectively) has no influence on the activity. In these cases the activity is likely to be limited by oxygen mass transfer. At lower glucose throughputs, the oxygen limitation seems to wane. Thus, the amounts of glucose oxidized are different in Section 9 (38 mmol h^{-1}) and 10 (43 mmol h^{-1}), where the glucose throughput is only half as much, i.e., 47 mmol h^{-1}. At low glucose throughputs and high conversions, the reaction is shifted towards the kinetic regime in which the activity is influenced by the glucose concentration. Baatz et al. showed that in the kinetic regime the specific activity rises with increasing glucose concentration [11]. Consistent to their results, the comparison between Sections 5 and 6, both with a retention time of 4 h, shows an increase of activity of about 30% by increasing the glucose feed concentration from 250 to 500 mmol l^{-1}, i.e., glucose reactor concentrations of 50 or 240 mmol l^{-1}, respectively. This activity increase would be even higher if the reaction was not limited by the oxygen supply at the higher glucose concentration.

During the 70-day run-time, the reactor efflux was always a clear, colourless aqueous solution, which contained in varying amounts sodium gluconate as sole product and non-converted glucose. Depending on the settings glucose conversions up to 96% were established during the run-time (Table 1). The separation of sodium gluconate from the reactor efflux should be simple and may be achieved by common techniques such as ion exchange or electro-dialysis. The non-converted glucose may be recirculated. Such simple post-processing is clearly an

advantage of this gold catalysed oxidation over the biotechnological process, in which extensive separation/purification steps are necessary.

The alumina-supported gold catalyst showed no loss of activity and selectivity at varying reaction conditions after these 70 days of continuous-flow glucose oxidation. During this time 72 mol of glucose were converted with 3.75 mg gold to give 15.7 kg sodium gluconate as a sole product. Extrapolated for 1 g gold, about 4.2 t sodium gluconate would have been produced, leading to estimated gold costs for the production of 1 kg sodium gluconate of less than 0.3€-Cent.

The excellent long-term stability and high selectivity of the gold catalyst shows that such catalysts are suitable for industrial carbohydrate oxidation processes. Here, not only the production of gluconic acid but also the production of other aldonic acids, e.g., maltobionic acid or lactobionic acid, which are not available in large quantities so far, could be achieved.

4. Conclusions

For the first time, a continuous-flow liquid-phase oxidation using a gold catalyst is described in this paper. A 0.25% Au/Al_2O_3 catalyst was investigated in the continuous-flow carbohydrate oxidation using glucose as model compound. The continuous mode was enabled by the use of a CSTR with an ultrasonic separation system. The efficiency of the ultrasonic separator was 99% and complete separation was achieved by using an additional separation vessel.

Over 70 days, the gold catalyst showed no loss of activity or selectivity in glucose oxidation. This excellent long-term stability stresses the possibility for using such catalysts in industrial applications. Further long-term stability, kinetic and deactivation studies with different gold catalysts, e.g., prepared by the incipient wetness method, are under investigation in continuous-flow glucose oxidation.

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