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Long-term stability of an Au/Al_2O_3 catalyst prepared by incipient wetness in continuous-flow glucose oxidation

Nadine Thielecke *, Klaus-Dieter Vorlop, Ulf Prüße

Institute of Technology and Biosystems Engineering, Federal Agricultural Research Centre (FAL), Bundesallee 50, 38116 Braunschweig, Germany

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Abstract

A 0.3% Au/Al_2O_3 catalyst prepared by the incipient wetness (IW) method was investigated in the continuous-flow liquid-phase glucose oxidation. Therefore, a continuous stirred tank reactor (CSTR) system equipped with an ultrasonic separator was used. The continuous-flow glucose oxidation was carried out at 40 °C, pH 9 and 1 bar oxygen partial pressure. Residence time and glucose concentration were varied. The IW gold catalyst showed very high activity and selectivity to gluconic acid within its 110 days of operation and, thus, an excellent long-term stability. Even after severe microbial contaminations of the catalyst, its activity could be completely restored by in situ regeneration with 2-propanol.

Keywords: Gold catalyst; Glucose oxidation; Gluconic acid; Incipient wetness; Continuous-flow oxidation; Liquid phase

1. Introduction

Gold catalysts show excellent activity and selectivity for the oxidation of aldoses [1–4]. This catalytic conversion enables the use of sugars as renewable resources for the production of high-value sugar acids. A very promising reaction is the oxidation of glucose to gluconic acid. Because of its good complexing properties and stability against hydrolysis at high temperatures and pH values, the biodegradable gluconic acid is used in the food and pharmaceutical industry as well as in paper and concrete production [5]. Today, gluconic acid and its derivatives are produced by biotechnological processes involving *Aspergillus niger* or *Gluconobacter suboxydans*. The annual worldwide production is estimated to be 100 000 t [6]. To be competitive to biotechnological processes the gold catalysts must fulfil important requirements for technical use like high activity, high selectivity and, especially, a high long-term stability.

The aim of this study was to check the long-term stability of a gold catalyst prepared by the incipient wetness (IW) method for the oxidation of glucose to gluconic acid under continuous-flow conditions.

2. Experimental

2.1. Catalyst preparation

The gold catalyst is prepared by the incipient wetness (IW) method as follows. Ten grams of alumina Puralox SCFa-90 (Sasol, Germany), doped with 0.3% sodium oxide [7], were used as support material. An acidic aqueous solution of 0.03 mol l^{-1} $HAuCl_4$ (Chempur, Germany) equal to the pore volume of the support, i.e. 0.5 ml g^{-1}, was added drop-wise to the support during intensive mixing. Afterwards, the precursor was dried overnight at 80 °C and activated by reduction in a hydrogen/nitrogen gas stream (2 l min^{-1}, 5% H_2) at 220 °C for 2 h. The gold content of the final catalyst is equal to 0.3 wt.% which was confirmed by ICP/OES. The catalyst was sieved prior to its use in the continuous-flow glucose oxidation. Only the fraction with particle diameter of 25–63 μm has been used in order to facilitate its separation by the ultrasonic separator under continuous-flow conditions.

2.2. Continuous-flow glucose oxidation

The CSTR for continuous-flow glucose oxidation 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

* Corresponding author. Tel.: +49 531 596 4266; fax: +49 531 596 4199.
E-mail address: nadine.thielecke@fal.de (N. Thielecke).

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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 5 min 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 resonator chamber of the ultrasonic separator (separation efficiency 99%). 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). The catalyst particles, which are discharged from the ultrasonic separator, sediment in the separation vessel and are pumped back into the reactor once every hour by a diaphragm pump (Electronic E2001, Prominent, Germany). 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 ±2%. As the reactants and the separation vessel are not thermostatted, the temperature inside the reactor varies within ±1 K as well.

The continuous-flow glucose oxidation is carried out at 40–60 °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. Accordingly, sodium gluconate, instead of gluconic acid, is the product of glucose oxidation. The glucose feed concentration (D-glucose, Merck, Germany) was varied between 500 and 750 mmol l^{-1} and the residence time was set between 6 and 10 h. 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 98.5% during the whole experiment, the specific activity could be calculated directly from the consumption of NaOH.

2.3. In situ catalyst regeneration

Two in situ catalyst regeneration methods have been used to stop microbial growth, disinfection by 2-propanol or heating. Disinfection by 2-propanol was carried out by changing the feed from glucose to water and afterwards to 2-propanol (70 vol.%) for 12 h. Subsequently, the feed was changed back to glucose via water. During that time, the pH-control and the oxygen supply were switched off. Disinfection by heating was carried out by switching the feed from glucose to water and heating the CSTR and the feed to 70 °C for 10 h. After decontamination, glucose oxidation was continued at 40 °C.

3. Results and discussion

Recently, we showed that it is possible to produce small gold particles (1.2–2 nm) supported on alumina by the incipient wetness method [7,8]. These catalysts showed high activity and selectivity for the oxidation of glucose to gluconic acid in batch experiments. This is very surprising as this preparation method has not been considered to be suitable for the production of active gold catalysts before [9–11] due to the resulting large gold particles (>10 nm). The aim of this study was to test the long-term stability of the active IW gold catalysts under continuous-flow conditions. Therefore, the CSTR system was used which has already been applied to test the long-term stability of an Au/Al_2O_3 catalyst prepared by deposition–precipitation with urea [12].

The continuous-flow glucose oxidation on an IW gold catalyst was maintained for 110 days. The specific activity during this run-time is shown in Fig. 1, in which the glucose feed concentration, the retention time and the average conversion are also mapped. The "noise" of the activity curve is caused by temperature and volume fluctuations as described above. Peaks occur, when settings, the pH-electrode or pump hoses have been changed.

The starting parameters of 500 mmol l^{-1} glucose feed concentration and 8 h residence time resulted in an average activity of 140 mmol min^{-1} g_{Au}^{-1}. This led to an average conversion of 90%. These conditions for continuous-flow glucose oxidation were kept for 40 days. During this period, the reactor efflux was a clear, colourless aqueous solution which contained non-converted glucose and sodium gluconate as the sole product. During the first 40 days, the activity curve shows some unsteadiness between Days 10 and 27. These variations are caused by a replacement of the glass frit for oxygen supply (Day 10), an interruption of the NaOH supply (Day 19) and two electrical power blackouts (Days 23 and 26). During NaOH interruption, the pH decreased to 7 and the reaction practically stopped, but restarted immediately after pH 9 was readjusted. The electrical power blackouts caused a complete switch off of the CSTR including all pumps, thermostatting, oxygen supply and pH control. No matter what system failure occurred, the

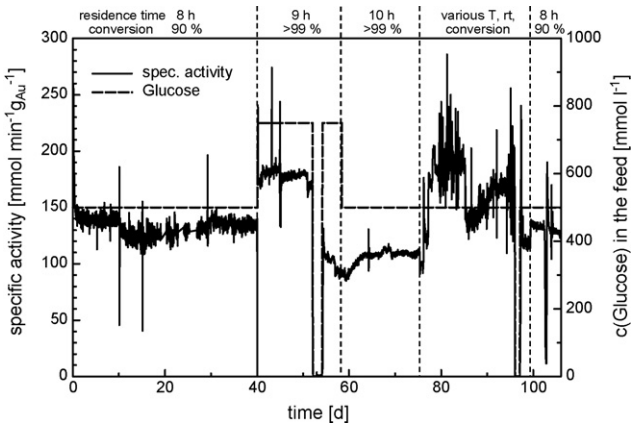

Fig. 1. Glucose feed concentration and specific activity of the 0.3% Au/Al_2O_3 catalyst at different retention times and resulting average conversions during continuous-flow glucose oxidation.

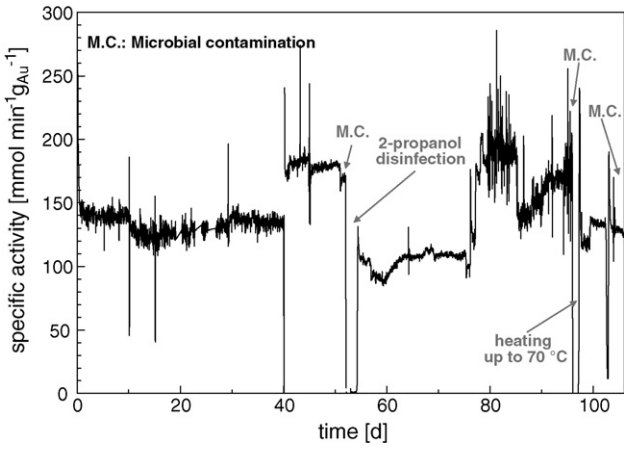

Fig. 2. Microbial contamination and in situ regeneration of the 0.3% Au/Al_2O_3 catalyst during continuous-flow glucose oxidation.

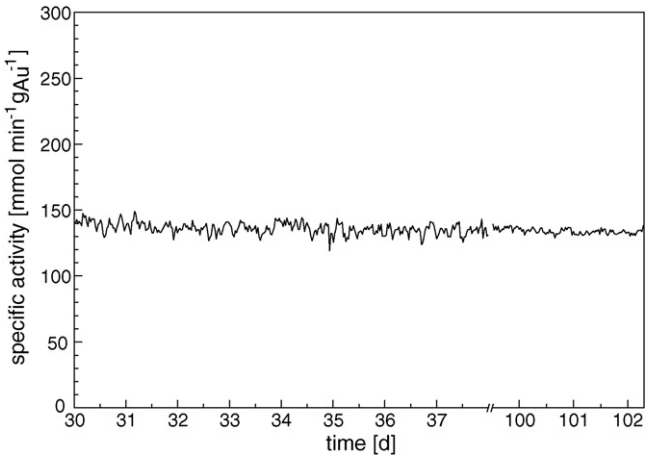

Fig. 3. Specific activity of the 0.3% Au/Al_2O_3 catalyst at equal reaction conditions after 30 and after 100 days of operation (c (glucose) in the feed 500 mmol l^{-1}, residence time 8 h).

same constant activity was observed after the reaction conditions were readjusted.

Further on, the influence of high gluconate concentrations on the gold catalyst was studied. Therefore, the glucose feed concentration and the residence time were increased (c (glucose) in the feed 750 mmol l^{-1}, residence time 9 h). A high and very stable conversion of over 99% was reached. Unfortunately, the reactor efflux became slightly turbid after 52 days of operation, which was a sign of microbial contamination. As glucose and gluconate are highly biodegradable, and the CSTR system operates under mild and non-sterile conditions, microbial growth is probable after some days of operation. The dates of microbial contamination are marked in Fig. 2. The microbial contamination did not only occur in the solution but also on the porous catalyst itself. Hence, an in situ disinfection of the system was necessary, which was carried out by 2-propanol. Afterwards the feed was changed back to glucose and the reactor efflux turned back into a clear, colourless solution. Hence, the decontamination with 2-propanol was successful and no observable microbial growth occurred during the next 42 days.

From Days 58 to 75, the glucose feed concentration was set to 500 mmol l^{-1} and the residence time was 10 h. The unusually long period of 5 days to reach steady state probably resulted from impurities caused by the microorganisms which have to be flushed out of the reactor. The slightly lower activity of 110 mmol l^{-1} g_{Au}^{-1} during this period, compared to the first 40 days, is consistent with the higher residence time and with the resulting higher glucose conversion.

To check if higher temperatures would inhibit the microbial growth, the temperature was increased at various residence times from Days 76 to 96. Temperatures of 60, 55 and 50 °C were adjusted but were accompanied by substantial fluctuation leading to an increased noise in the activity curve. Although these high temperatures were assumed to be suitable to inhibit microbial growth, a new microbial contamination occurred at Day 96, leading again to a slightly turbid efflux. This time, an in situ disinfection of the system was carried out by heating. Although the efflux cleared after this high temperature treatment, the microbial growth started again after a few days. This time the growth accelerated and the run had to be terminated. Obviously, the temperature treatment was less effective for in situ catalyst regeneration than using 2-propanol.

Between the second and the third microbial contaminations, starting conditions were readjusted (40 °C, c (glucose) in the feed 500 mmol l^{-1}, residence time 8 h) for 3 days to find out whether any of the failures had influenced the catalytic activity. As shown in Fig. 3, from Days 99 to102 an activity is reached which is equal to the activity of the first 40 days of operation. The microbial contamination as well as the in situ regeneration with 2-propanol and temperature did not affect the catalytic activity and selectivity of the IW gold catalyst. Thus, the catalyst can be described as an exceptionally stable and robust catalyst which shows an excellent long-term stability for continuous-flow glucose oxidation.

4. Conclusions

A gold catalyst supported on alumina and prepared by incipient wetness was used in continuous-flow glucose oxidation. The IW gold catalyst showed a very high activity and selectivity to gluconic acid within its 110 days of operation and, thus, an excellent long-term stability. Even after severe microbial contaminations of the catalyst, its activity could be completely restored by in situ regeneration with 2-propanol. During the time of operation, 4 t gluconic acid per gram gold were produced with this catalyst without any loss of activity or selectivity. Thus, oxide supported gold catalysts are robust and exceptionally stable for liquid-phase glucose oxidation over the long-term, and therefore fulfil all important requirements for their technical use.

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