Catalytic conversion of renewables: Kinetic and mechanistic aspects of the gold-catalyzed liquid-phase glucose oxidation

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Abstract

Among the studies about conversion of renewable resources, glucose oxidation to gluconic acid received very much attention in recent years. The present paper describes kinetic and mechanistic aspects of the liquid-phase glucose oxidation. Therefore a 0.3 % Au/Al_2O_3 catalyst prepared by the incipient wetness method was used. The reaction conditions were varied between 20 to 60 °C, pH 7 to 10, catalyst concentrations between 50 to 1200 mg l^{-1} and initial glucose concentrations between 10 to 1000 mmol l^{-1}. The concentration of dissolved oxygen was tracked for most experiments. An increasing activity was found with increasing pH value in the range between pH 7 and 10, and with increasing temperature in the range between 20 and 60 °C, whereas the selectivity to gluconic acid remained unchanged at > 99 % under these conditions. The activation energy was determined to be 53 kJ mol^{-1}. Analysis of the reaction orders with regard to glucose and oxygen leads to the conclusion that the Eley-Rideal model proposed by Beltrame et al. (2006) should be discarded for the gold-catalyzed glucose oxidation. Hydrogen peroxide is formed as by-product in glucose oxidation under oxygen atmosphere, whereas hydrogenated products are by-products under oxygen-free conditions. These observations have been explained by a modified oxidative dehydrogenation mechanism.

Keywords: conversion of renewables, gold catalyst, glucose oxidation, kinetics, mechanism

Zusammenfassung

Katalytische Konversion nachwachsender Rohstoffe: Kinetische und mechanistische Aspekte der goldkatalytisierten Glucoseoxidation in der Flüssigphase

Im Bereich der katalytischen Konversion nachwachsender Rohstoffe hat die goldkatalysierte Glucoseoxidation in den letzten Jahren besondere Aufmerksamkeit erlangt. Hier werden kinetische und mechanistische Aspekte der Glucoseoxidation anhand eines Aluminiumoxid-geträgerten 0,3 %igen Goldkatalysators, der nach der incipient wetness-Methode hergestellt wurde, beschrieben. Für die kinetischen Untersuchungen wurden Untersuchungen bei 20 bis 60 °C, pH 7 bis 10, einer Katalysatorkonzentration von 50 bis 1200 mg L^{-1} und einer Ausgangsglucosekonzentration von 10 bis 1000 mmol L^{-1} durchgeführt. Zusätzlich wurde die Gelöstauerstoffkonzentration bei zahlreichen Experimenten verfolgt. Mit steigendem pH-Wert und steigender Temperatur wurde eine Zunahme der Aktivität bei einer gleichbleibend hohen Selektivität von > 99 % festgestellt. Im untersuchten Temperaturbereich beträgt die scheinbare Aktivierungsenergie 53 KJ mol^{-1}. Die Analyse der Reaktionsordnungen in Bezug auf Glucose und Sauerstoff zeigt, dass ein Reaktionsverlauf der Glucoseoxidation nach dem Eley-Rideal-Modell, wie er von Beltrame et al. (2006) für diese Reaktion vorgeschlagen wurde, nicht zutreffend ist. Wasserstoffperoxid konnte als Nebenprodukt der Glucoseoxidation unter Sauerstoffatmosphäre nachgewiesen werden, wohingegen unter Sauerstoffausschluss auch hydrierte Produkte gebildet werden. Durch einen modifizierten Mechanismus der oxidativen Dehydrogenierung konnten beide Beobachtungen erklärt werden.

Schlüsselworte: Katalytische Konversion nachwachsender Rohstoffe, Goldkatalysator, Glucoseoxidation, Kinetik, Mechanismus

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1. Introduction

The conversion of renewable resources to valuable products of the chemical industry is an attractive way to save fossile resources and CO_2 emissions endangering global climate. Among the biomass carbohydrates glucose is the most abundant bio-feedstock for this purpose. In this regard, the metal-catalyzed liquid-phase oxidation of glucose to gluconic acid by gold nanoparticles has received much attention during very recent years. As first described by Biella et al. (2002), gold nanoparticles in the range of 2 to 5 nm supported on carbon show a much higher activity under mild reaction conditions than the conventional platinum and palladium based catalysts applied so far for this reaction. Further on, the Au/C catalyst exhibits an outstanding selectivity of 100 % towards gluconic acid, a fine chemical with an annual worldwide production capacity of about 100,000 tons (Lichtenthaler, 2006), currently exclusively produced by biocatalytic glucose oxidation.

The majority of the studies on gold-catalyzed glucose oxidation used carbon-supported gold nanoparticles originating from preformed gold sols (Biella et al., 2002; Önal et al., 2004; Comotti et al., 2005; Comotti et al., 2006a and b), polymer-stabilized gold colloids (Mirescu and Prüße, 2006), glucose-stabilized gold sols (Beltrame et al., 2006) or gold colloids in "naked" form (Comotti et al., 2004; Comotti et al., 2006c). In some of these studies (Beltrame et al., 2006; Comotti et al., 2004; Comotti et al., 2006b) the activity of the gold nanoparticles have been described as lower but comparable to the activity of the enzyme used in the technical processes for the production of gluconic acid (Beltrame et al., 2004). Taking into account the outstanding almost 100 % selectivity of the gold nanoparticles, which saves additional purification expenses, an industrial gold-catalyzed glucose oxidation process seems to be within range. Unfortunately, gold colloids, as well as carbon-supported gold nanoparticles derived from preformed sols, do not fulfil the major requirement for a catalyst to be used in an industrial process: a high long-term stability. The naked colloids agglomerate after a few minutes so that complete conversion can not be reached (Comotti et al., 2006c), and a chitosan-stabilized colloid precipitated in flakes has been described to lose about 90 % of its initial activity after eight repeated batches (Mirescu and Prüße, 2006). Also the carbon-supported gold nanoparticles originating from preformed sols do not perform much better as they lose about 50 % or 60 % of their initial activity within 4 or 5 repeated batches, respectively (Biella et al., 2002; Comotti et al., 2006b).

However, highly active, almost 100 % selective and long-term stable gold catalysts for the liquid-phase carbohydrate oxidation can be obtained by using metal oxides as support material, e.g. Al_2O_3 or TiO_2 prepared either by deposition-precipitation with NaOH or urea or by the incipient wetness method (Baatz and Prüße, 2007; Baatz et al., 2007; Mirescu and Prüße, 2007; Mirescu et al., 2007; Thielecke et al., 2007a and b). These catalysts have been used for the oxidation of glucose and various other aldoses to their corresponding aldonic acids in repeated batch experiments as well as partially under continuous-flow conditions. No matter which catalyst or reaction conditions were applied, the metal oxide-supported gold catalysts always showed a high activity, nearly 100 % selectivity and, as no activity and selectivity loss occurred, a high long-term stablility. Hence, gold nanoparticles supported on metal oxides fulfil all necessary requirements for their application in an industrial carbohydrate oxidation process to produce various aldonic acids, e.g. gluconic acid.

Knowledge about the reaction kinetics of the gold-catalyzed glucose oxidation is very important with regard to an up-scaling of the process to industrial scale. Thus far, only few studies about glucose oxidation reaction kinetics with gold catalysts are available (Beltrame et al., 2006; Önal et al., 2004). In one study carbon-supported gold nanoparticles derived from preformed gold sols have been used (Önal et al., 2004) whereas glucose-stabilized gold colloids have been used in the other one (Beltrame et al., 2006).

Surprisingly, contrary results have been obtained in these two studies. Önal et al. (2006) reported that the reaction follows the Langmuir-Hinshelwood model in which both glucose and oxygen are adsorbed. They found only a negligible increase of the initial reaction rate with rising initial glucose concentration, but a distinct selectivity decrease. Beside glucose isomerisation products such as mannose and fructose, and degradation products such as the oxygenated C3-bodies glycerolaldehyde or dihydroxyacetone, also the hydrogenated product sorbitol, have been found. The latter product gives strong evidence that the reaction follows the oxidative dehydrogenation mechanism well known for the liquid-phase noble metal-catalyzed oxidation of alcohols and aldehydes (Besson and Gallezot, 2001a and b; Gallezot and Besson, 1995; Mallat and Baiker, 1994).

In contrast to these findings, Beltrame et al. (2006) reported about an increase of the initial reaction rate with rising initial glucose concentration tending to an asymptote at higher glucose concentration. This result, together with an experimentally derived reaction order of 1 for oxygen, has led to the assumption that the glucose oxidation follows the Eley-Rideal model in which dissolved oxygen reacts from the liquid phase with glucose adsorbed at the catalyst surface. However, the Eley-Rideal model suggested by Beltrame et al. (2006) is in contradiction to another study of the same group. Comotti et al. (2006c) proposed a new reaction mechanism for glucose oxidation, which is different from the oxidative dehydrogenation mecha-

nism, but able to explain the experimentally determined intermediate formation of hydrogen peroxide. According to this mechanism both glucose and oxygen are adsorbed at the catalyst surface at the same time.

The contrary kinetic models reported in the two studies are based on the dependence of the reaction rate on the initial glucose concentration, which has been studied only in a small range of glucose concentrations, i.e., 100 to 450 mmol l^{-1} by Önal et al. (2004) and 50 to 500 mmol l^{-1} by Beltrame et al. (2006). It has already been pointed out that 'the experimental evidence is hardly sufficient to support that differentiation' (Bond et al., 2006).

In the present study, reaction kinetics of the liquid-phase glucose oxidation using an 0.3 % Au/Al_2O_3 catalyst at 1 bar oxygen pressure is examined. The activity and selectivity of the catalyst has been further studied in dependence of the catalyst concentration, pH value, temperature and initial glucose concentration from 10 mmol l^{-1} up to 1000 mmol l^{-1}. This larger concentration span should give more significant results compared to the other two kinetic studies. Particular care has been taken to avoid oxygen mass transfer limitation by monitoring the dissolved oxygen concentration during the course of reaction whenever possible. Reaction orders have been analyzed for glucose and oxygen, and the activation energy is reported. Finally, basing on own experiments and literature data, a modified oxidative dehydrogenation mechanism for the gold-catalyzed glucose oxidation is proposed which takes the formation of hydrogen peroxide into account.

2. Experimental

2.1 Chemicals

Powdered mesoporous aluminium oxide type Puralox KR-90 from Sasol, Germany, (BET surface area = 88 m^2 g^{-1}, pore volume = 0.63 ml g^{-1}, mean particle size = 40 µm) was used as support material and $HAuCl_4 \cdot xH_2O$ (gold content 50 wt %) from Chempur, Germany, as the gold precursor. D(+)-glucose monohydrate (for biochemical use) from Fluka, Germany, and KOH (purity 86 %) from Fluka, Germany, were used as supplied. Technical oxygen (purity 99.95 %) from Linde, Germany, was used as an oxidant without further purification.

2.2 Catalyst preparation

The gold catalyst used in the present study was prepared by the incipient wetness method according to the following procedure: A volume of an acidic aqueous solution of $HAuCl_4$ in the desired concentration, which corresponds to the pore volume of the alumina support, was added drop-wise within 15 min to the support material during intensive mixing in a mortar. At the end of this procedure the catalyst precursor becomes slightly wet. After the precursor was dried overnight at 75 °C in air, it was reduced for 2 h at 250 °C in a 10 vol% H_2/90 vol% N_2 stream. ICP-AES analysis confirmed a gold content of 0.3 %.

2.3 Glucose oxidation procedure

Glucose oxidation was carried out in a thermostatted glass reactor (total volume 600 ml, initial reaction volume 500 ml) equipped with a reflux condenser, a pH electrode and a burette for base dosage, a glass frit for the oxygen supply, an oxygen electrode, a gas outlet and a magnetic stirrer which operated at 900 rpm.

Prior to the start of the reaction the desired catalyst amount was suspended in 450 ml of deionized water at the desired pH value inside the reactor. This suspension was thermostatted until the reaction temperature was reached, while oxygen at atmospheric pressure was bubbled through the suspension at a flow rate of 500 ml min^{-1} to saturate the suspension with dissolved oxygen. A reaction was started by first adding the desired amount of glucose dissolved in 30 ml of deionized water thermostatted at the reaction temperature and afterwards 20 ml of deionized water used for rinsing to ensure that all glucose had been added to the reactor. At initial glucose concentrations of 500 mmol l^{-1} and 1000 mmol l^{-1}, the catalyst was suspended in a smaller amount of water, as more water was needed to dissolve the larger amounts of glucose.

During the reaction the oxygen supply was maintained at the same flow rate and the pH value was kept constant with an automatic titrator (TitroLine alpha, Schott, Germany) by adding aqueous KOH in concentrations between 0.25 mol l^{-1} and 10 mol l^{-1} depending on the initial glucose concentration used. In different sets of experiments, one of the parameters: catalyst concentration, pH value, temperature or initial glucose concentration was varied, while the others, unless otherwise stated, were fixed at the standard reaction conditions, i.e., 140 mg l^{-1} catalyst concentration, pH 9, 40 °C, 100 mmol l^{-1} initial glucose concentration. During reaction course, the amount of added KOH and, when possible (see Section 2.4), the concentration of dissolved oxygen were monitored. All reactions were carried out until a conversion > 99 % was reached. Conversion and selectivity were checked with a HPLC system as previously reported (Baatz et al., 2007; Mirescu and Prüße, 2007).

2.4 Dissolved oxygen

During the course of all reactions carried out up to 40 °C, which marks the highest application temperature of the oxygen measurement system, the concentration

of dissolved oxygen was tracked by an oxygen electrode (CellOx 325, WTW, Germany) in combination with a measuring instrument (Oxi 340i, WTW, Germany). All measured oxygen concentrations were normalized with regard to the highest oxygen concentration occurring during each reaction course (always after complete glucose conversion) and are reported as percentage of the maximum oxygen solubility at the end of the reaction.

The solubility of oxygen in the reaction suspension depends on the temperature, the glucose concentration and the salinity of the suspension. As displayed in Table 1, the influence of the temperature on the oxygen solubility is higher than the influence of the glucose concentration. The oxygen solubility values reported in Table 1 were calculated by using Henry constants interpolated from Henry constants for aqueous glucose solutions reported in the literature (Rischbieter et al., 1996) and assuming that the temperature dependence of oxygen solubility in aqueous glucose solutions corresponds to that of oxygen in water (Radtke et al., 1998).

Table 1:

Calculated concentrations of dissolved oxygen in the reaction suspension at 1 bar oxygen pressure in dependence of the initial glucose concentration and temperature

$c_{0,\ glucose}$ mmol l^{-1}	Temperature °C	c_{oxygen} mmol l^{-1}
10	40	0.972
50	40	0.966
100	40	0.956
250	40	0.925
500	40	0.872
1000	40	0.766
100	20	1.350
100	30	1.122
100	40	0.956
100	50	0.825
100	60	0.728

If the concentration of dissolved oxygen is to be monitored during glucose oxidation, a problem emerges. The decreasing glucose concentration with proceeding conversion leads to an increasing oxygen solubility while the increasing salinity caused by the formation of the reaction product potassium gluconate leads to a decreasing solubility (Radtke et al., 1998). Both effects become significant at higher initial glucose concentrations, i.e., 500 mmol l^{-1} and 1000 mmol l^{-1}, and may lead to an estimated error with regard to the reported oxygen values of about 10 %.

2.5 Evaluation of catalytic activity

The gluconate versus time plots were derived from the rate of KOH addition. As, with HPLC analysis, a conversion and selectivity of > 99 % had been determined for all experiments reported here, the KOH addition rate directly corresponded to the glucose conversion and gluconate formation. A typical gluconate versus time plot is shown in Figure 1, in which, after a short induction period, a linear increase of the gluconate concentration up to about 80 % conversion can be noted before the reaction rate subsequently decreases towards complete conversion. As indicated by the fit line in Figure 1, the linear part of the curve was used to calculate the activity from the slope of the fit line. Further on, the activity is referred to the gold content of the catalyst, so that it is given in terms of mmol of produced gluconate per minute and per gram gold, i.e., mmol min^{-1} g_{Au}^{-1}.

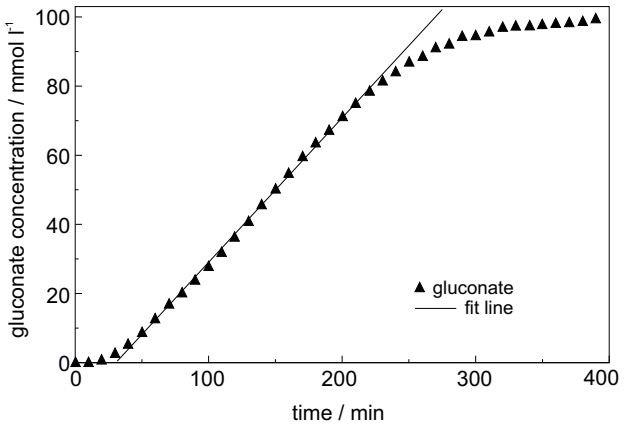

Figure 1:

Typical gluconate versus time plot. The slope of the fit line in the linear part of the curve is used to calculate the activity of the catalyst. Reaction conditions: ccatalyst = 140 mg l^{-1}, $c_{0,\ glucose}$ = 100 mmol l^{-1}, 40 °C, pH 9.

2.6 Analysis of hydrogen peroxide

Hydrogen peroxide was analysed according to the procedure described by Comotti et al. (2006c). Therefore, the pH of the periodically withdrawn 10 ml samples was adjusted to 1.8 by adding 0.5 mol l^{-1} H_2SO_4. After addition of 0.5 ml $MnSO_4$ solution (c = 1 mmol l^{-1}) the samples were titrated with 20 mmol l^{-1} $KMnO_4$ solution.

2.7 Glucose oxidation under oxygen-free conditions

For this reaction the same equipment was used as described in 2.3. For the reaction, 100 mmol l^{-1} Glucose was first stirred with 10,000 mg l^{-1} catalyst at 40 °C at pH 9 for 24 h. After 24 h, the pH was adjusted to 10.5. These

conditions were maintained for another 60 h so that the whole reaction lasted 94 h. The pH value was kept constant at all times by titrating 2.5 mol l^{-1} KOH. Instead of oxygen, nitrogen (purity 99.999 %) was bubbled permanently through the suspension at a flow rate of 50 ml min^{-1} in order to secure oxygen-free conditions.

Analysis of the reaction mixture after 94 h was performed as described in section 2.3. The results were confirmed by an additional analysis carried out by Südzucker AG.

3. Results and discussion

For an analysis of reaction kinetics, mass transfer limitations have to be excluded. To exclude pore diffusion, a finely powdered catalyst support was used and a low gold loading was adjusted to the catalyst. To exclude external mass transfer limitations a high stirring rate of 900 rpm was applied. As oxygen, due to its low solubility, is the deficit compound in glucose oxidation (see Table 1) a sufficient concentration of dissolved oxygen during the reaction course has to be ensured by adjusting a proper catalyst concentration.

3.1 Influence of catalyst concentration

To figure out the influence of the catalyst concentration on the apparent reaction rate and the amount of dissolved oxygen during the reaction course, catalyst concentrations from 50 to 1200 mg l^{-1} were used for glucose oxidation under otherwise standard reaction conditions (see Section 2.3).

The course of produced gluconate and the normalized oxygen concentration versus time are displayed in Figures 2 A and B for two catalyst concentrations. At the lowest applied catalyst concentration, i.e., 50 mg l^{-1}, which is shown in Figure 2A, the concentration of dissolved oxygen during the reaction course remains almost constant at the saturation level. Thus, even at the highest reaction rate during this run, the rate of oxygen dissolution is higher than the rate at which oxygen is consumed by the reaction. In contrast, the second highest catalyst concentration applied here, i.e., 800 mg l^{-1}, leads to a dramatic decrease of the normalized oxygen concentration to below 10 % immediately after the reaction has started. After about 50 % glucose conversion, the oxygen concentration slowly starts to increase. A value of 50 % dissolved oxygen is reached at 90 % glucose conversion, and the saturation value of 100 % is not attained before complete glucose conversion. Needless to say that such a pronounced decrease in dissolved oxygen significantly influences the activity of the catalyst.

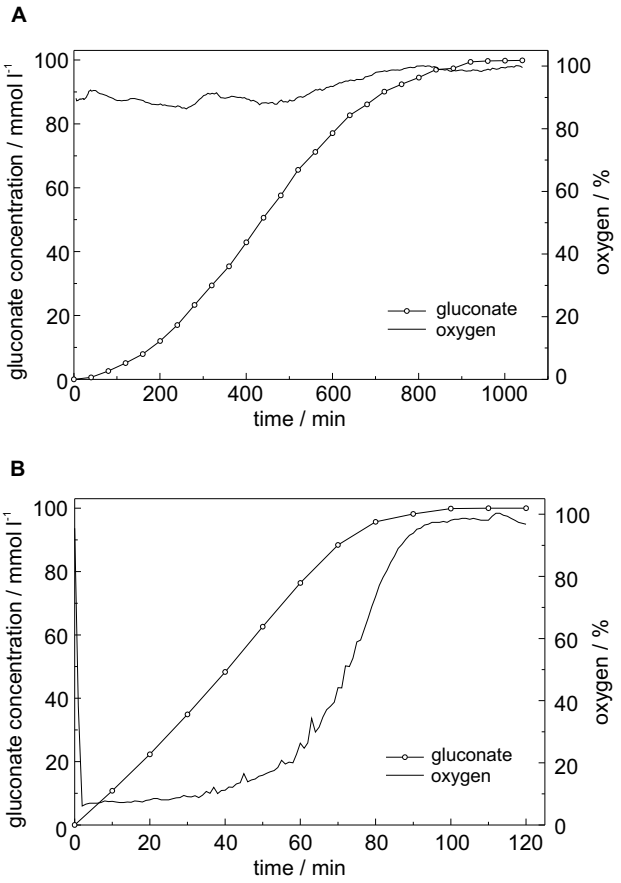

Figure 2:
Gluconate and normalized oxygen concentration versus time plots for a catalyst concentration of A: 50 mg l^{-1} and B: 800 mg l^{-1}. Other reaction conditions: $c_{0,\,glucose}$ = 100 mmol l^{-1}, 40 °C, pH 9.

The reaction rate of glucose oxidation in dependence of the applied catalyst concentration is depicted in Figure 3. As expected, the reaction rate tends to be an asymptote at high catalyst concentration when an external mass transfer limitation becomes apparent, whereas a linear increase, i.e., no external mass transfer limitation, can be observed up to a catalyst concentration of about 200 mg l^{-1}. For some of the applied catalyst concentrations the course of the normalized oxygen concentration versus glucose conversion is additionally displayed in Figure 4. It can clearly be noted that the oxygen concentration drops considerably with rising catalyst concentration. Lowest oxygen concentrations at a single catalyst concentration can be found at between 10 % and 50 % glucose conversion, when the observed reaction rate is highest for all catalyst concentrations. At a catalyst concentration of 140 mg l^{-1}, a concentration at which the results shown in Figure 3 confirm no mass transfer limitation, the oxygen concentration over the whole glucose conversion drops down to 60 % at maximum (Figure 4). At the higher catalyst concentration of 400 mg l^{-1}, a concentration at which the results

shown in Figure 3 clearly indicate beginning mass transfer limitations, the oxygen concentration drops down to about 40 % during the first 50 % of glucose conversion (Figure 4). It can thus be concluded that the normalized oxygen concentration should not fall below 50 % at any time during the reaction course in order to avoid oxygen mass transfer limitations.

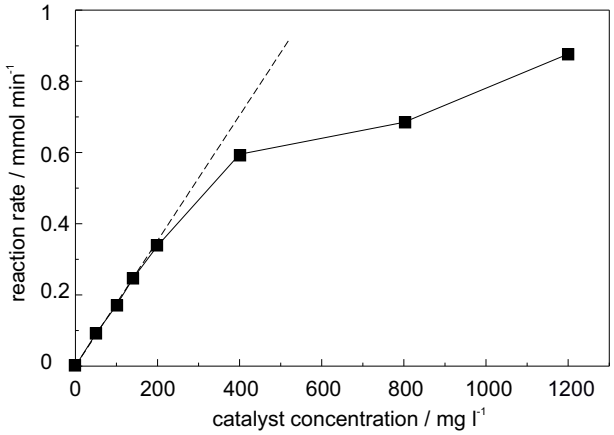

Figure 3:

Influence of the applied catalyst concentration on the apparent reaction rate. The dashed line indicates the reaction rate without external oxygen mass transfer limitation. Other reaction conditions: $c_{0,\ glucose}$ = 100 mmol l^{-1}, 40 °C, pH 9.

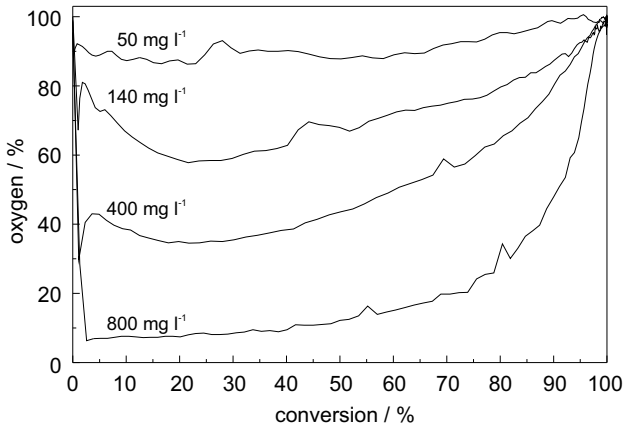

Figure 4:

Plot of the normalized oxygen concentration versus glucose conversion at four different applied catalyst concentrations. Other reaction conditions: $c_{0,\ glucose}$ = 100 mmol l^{-1}, 40 °C, pH 9.

3.2 Influence of the pH value

The influence of the pH value on glucose oxidation was studied in the range between pH 7 and pH 10. At the lower pH values of 8 and 7, a higher catalyst concentration of 280 mg l^{-1} or 420 mg l^{-1}, respectively, was used in order to compensate for the expected lower activity. Otherwise, standard reaction conditions were used. For all different runs the concentration of dissolved oxygen was monitored and assured to be higher than 50 %.

The results depicted in Figure 5 show the expected rising activity with increasing pH value. This finding is consistent with results reported for glucose oxidation on various other gold catalysts (Biella et al., 2002; Comotti et al., 2006b; Mirescu et al., 2007; Önal et al., 2004). The selectivity to gluconate always exceeded 99.5 % within the pH range studied here. At pH values higher than 10, the selectivity decreases mainly due to the formation of the alkali-promoted isomerisation products fructose and mannose as already reported in (Biella et al., 2002; Mirescu et al., 2007; Önal et al., 2004). Thus, pH values higher than 10 were not considered in this study. Likewise, glucose oxidation at pH values lower than 7 were not examined due to the expected very low activity. Low activities under neutral or slightly acidic pH values have also been described for the glucose oxidation with other noble metal catalysts based on palladium or platinum, which mainly has been ascribed to a catalyst poisoning by adsorbed free gluconic acid (Besson and Gallezot, 2001a; Mallat and Baiker, 1994).

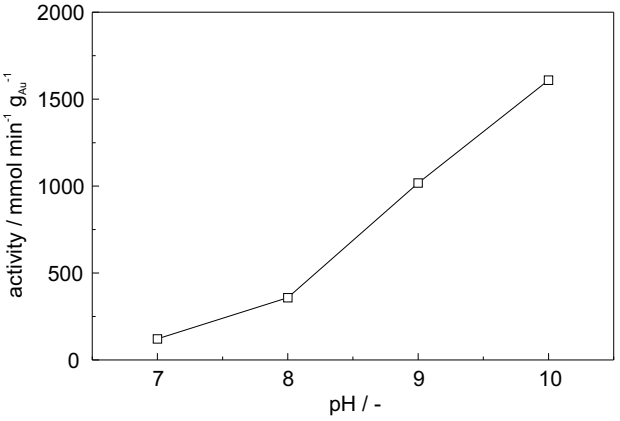

Figure 5:

Influence of the pH value on the catalyst activity. Other reaction conditions: $c_{catalyst}$ = 420 mg l^{-1} at pH 7, $c_{catalyst}$ = 280 mg l^{-1} at pH 8, $c_{catalyst}$ = 140 mg l^{-1} at pH 9 and 10, $c_{0,\ glucose}$ = 100 mmol l^{-1}, 40 °C.

3.3 Influence of the temperature

The influence of the temperature on the glucose oxidation was checked within a range between 20 °C and 60 °C. The concentration of dissolved oxygen was monitored only up to a temperature of 40 °C as the applied oxygen electrode has an upper application temperature of 45 °C. During the runs at 20 °C, 30 °C and 40 °C, the normalized oxygen concentration always exceeded 60 % so that external mass transfer limitations were excluded.

The catalyst activity in dependence of the reaction temperature is reported in Table 2. As expected, the activity values strongly increase with increasing reaction tempera-

ture, a finding which is consistent with those of Comotti et al. (2006b), Beltrame et al. (2006) and Mirescu et al. (2007) for the same reaction but other types of gold catalysts. In the temperature range studied here, the selectivity was not affected by the temperature and always exceeded 99 %. In order to achieve a high selectivity, temperatures higher than 60 °C are generally not advisable for carbohydrate oxidation as homogeneous reactions such as isomerisation and various degradation reactions leading to brown products are favoured at such high temperatures as already reported for the oxidation of glucose (Mirescu et al., 2007; Önal et al., 2004) as well as for maltose and lactose (Mirescu and Prüße, 2007).

Table 2:

Temperature dependency of the catalyst activity for glucose oxidation. Other reaction conditions: pH 9, $c_{0,\ glucose}$ = 100 mmol l^{-1}, $c_{catalyst}$ = 140 mg l^{-1}.

Temperature °C	Activity mmol min^{-1} g_{Au}^{-1}
20	194
30	285
40	1173
50	1517
60	2165

Within the temperature range between 30 °C and 60 °C, Beltrame et al. (2006) determined an apparent activation energy of 47 kJ mol^{-1} for glucose oxidation on their glucose-stabilized gold colloid. For the present study the Arrhenius plot based on the activities shown in Table 2 is displayed in Figure 6. It shows an apparent activation energy of 53 kJ mol^{-1} for the 0.3 % Au/Al_2O_3 catalyst used here which is in good consistence with Beltrame et al. (2006).

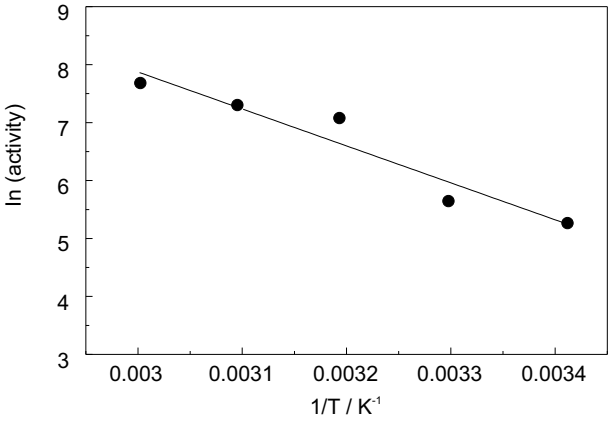

Figure 6:

Arrhenius plot for the determination of the activation energy

3.4 Influence of the initial glucose concentration

The dependence of the reaction rate on the initial glucose concentration has, thus far, only been studied in small concentration ranges, i.e. 100 to 450 mmol l^{-1} by Önal et al. (2004) and 50 to 500 mmol l^{-1} by Beltrame et al. (2006). Further on, the fits of the rate vs. concentration curves in both studies appear quite risky, as are the stated contrary reaction models, i.e., the Langmuir-Hinshelwood model by Önal et al. (2004) or the Eley-Rideal model by Beltrame et al. (2006), deduced from these curves, a point which has already been criticized by Bond et al. (2006).

Hence, a more significant span of initial glucose concentrations, ranging from 10 to 1000 mmol l^{-1} was examined in the present study under otherwise standard reaction conditions. The concentration of dissolved oxygen was tracked for all initial glucose concentrations studied here. The gluconate vs. time together with the normalized oxygen concentration vs. time curves are depicted in Figure 7 for four different initial glucose concentrations. The normalized oxygen vs. time curves suggest no oxygen limitations up to 500 mmol l^{-1} initial glucose concentration, whereas a small oxygen limitation may have occurred at 1000 mmol l^{-1}, as in the latter case the normalized oxygen concentration slightly falls below 50 %.

The catalyst activity in dependence of the initial glucose concentration is displayed in Figure 8 which shows an increasing activity with rising initial glucose concentration up to 500 mmol l^{-1}. At an initial concentration of 1000 mmol l^{-1} the activity is more or less equal to that at 500 mmol l^{-1}. The independence of the rate on the initial glucose concentration as reported by Önal et al. (2004) is not supported by the present results.

Analysis of the reaction order for glucose was carried out both by the differential and integral methods. Similar results were obtained with the two methods showing that the reaction order for glucose is equal to 0.5 as mean value over the whole concentration range studied. However, the integral analysis revealed a decreasing reaction order with increasing initial glucose concentration as it would be expected for a component which adsorbs at the catalyst surface.

3.5 Kinetic model and mechanistic aspects

The discrimination of the kinetic model should not rely solely on the basis of the rate dependence in the initial glucose concentration but should also take into account other reactants. For the present study, the normalized oxygen concentrations shown for different catalyst concentrations in Figure 4 are used to estimate the influence of the dissolved oxygen concentration on glucose oxidation at otherwise equal conditions.

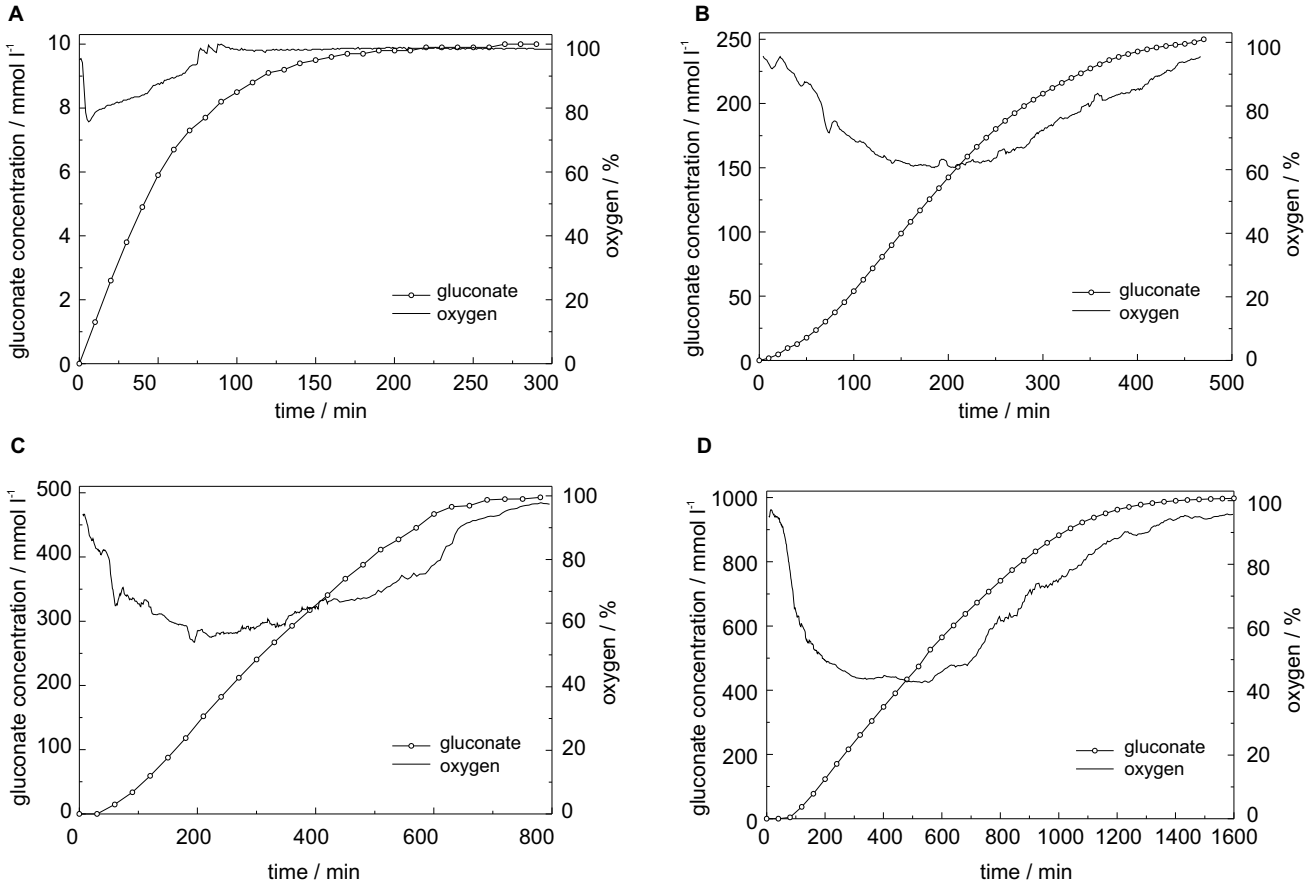

Figure 7:

Gluconate and normalized oxygen concentration versus time plots for an initial glucose concentration of A: 10 mmol l^{-1}, B: 250 mmol l^{-1}, C: 500 mmol l^{-1} and D: 1000 mmol l^{-1}. Other reaction conditions: $c_{catalyst}$ = 140 mg l^{-1}, 40 °C, pH 9.

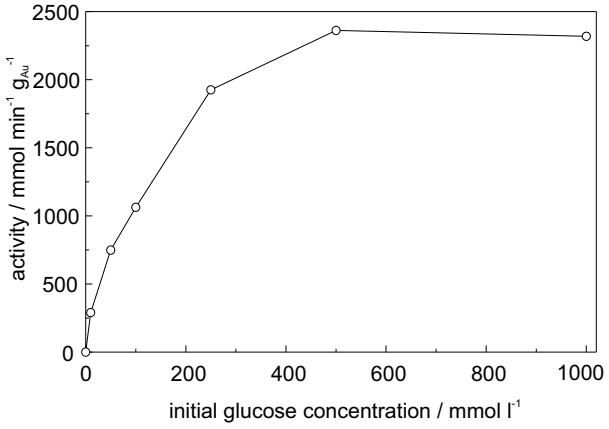

Figure 8:

Influence of the initial glucose concentration on the catalyst activity. Other reaction conditions: $c_{catalyst}$ = 140 mg l^{-1}, 40 °C, pH 9.

Therefore, the catalyst activity in dependence of the medium normalized oxygen concentration between 10 and 50 % glucose conversion, i.e., at the highest reaction rate, was analyzed by the differential method ($\log_{activity}$ vs. $\log_{oxygen}$ plot). The slope of the fit line, which corresponds to the reaction order of oxygen, lies at a value of about 0.35 suggesting that oxygen adsorption and reaction from the adsorbed state is likely. This value is definitely different from 1, which is the oxygen reaction order proposed by Beltrame et al. (2006) on the basis of two different oxygen partial pressures. The oxygen reaction order of 1 has been used as further evidence for the Eley-Rideal model in that study, which the authors themselves describe as very uncommon for gold-catalyzed reactions.

The reaction order for glucose between 0 and 1 found in this study suggests glucose adsorption on the catalyst as well. Glucose reacting from the adsorbed state has likewise been proposed in the other kinetic studies (Beltrame et al., 2006; Önal et al., 2004). Consequently, as experimental evidence exists that both glucose and oxygen react at the catalyst surface, the Eley-Rideal model for the gold-catalyzed oxidation of glucose proposed by Beltrame et al. (2006) has to be discarded. Consequently, the gold catalyzed glucose oxidation is more likely to follow the Langmuir-Hinshelwood model.

An Eley-Rideal kinetic model also would not fit to the two reaction mechanisms for the gold-catalyzed glucose oxidation currently under discussion. On the one hand, this is the classic oxidative dehydrogenation mechanism which has already been proven for alcohol and carbohydrate oxidation on other noble metal catalysts, e.g., Pt and Pd, (see Gallezot and Besson, 1995; Besson and Gallezot, 2001b, and references therein). According to this mechanism, glucose is first hydrated to the geminal diol that dissociatively adsorbs at the catalyst surface, leading to adsorbed gluconic acid, which desorbs, and an adsorbed hydrogen atom. Adsorbed hydrogen atoms subsequently react with dissociatively adsorbed oxygen to adsorbed water which afterwards desorbs. If no oxygen is present the reaction nonetheless proceeds to a considerable extent.

On the other hand, Comotti et al. (2006c) have suggested a mechanism in which glucose is first attacked by hydroxide leading to the deprotonated geminal diol of glucose. This anionic hydrated glucose species adsorbs at the catalyst surface leading to an electron rich gold which facilitates oxygen adsorption by a nucleophilic attack. Elimination of a proton from the adsorbed glucose species, together with the transfer of another electron from this species to the co-adsorbed anionic oxygen species via gold, results in the gluconate anion and a peroxide-like oxygen species.

Both mechanisms have their strong points and weak points. The classic oxidative dehydrogenation mechanism is able to explain the formation of hydrogenated products, which have been described by Önal et al. (2004) for the gold-catalyzed glucose oxidation, as the catalyst surface is covered by reactive hydrogen species during the oxidation reaction. However, the observed activity rises with increasing pH value and the observed formation of hydrogen peroxide (Beltrame et al., 2006; Comotti et al., 2006c) can not be understood on the basis of this mechanism. In contrast, both the promoting effect of alkali and H_2O_2 formation can easily be understood by the Comotti mechanism. However, according to their mechanism, hydrogenated products can not be formed as the catalyst's surface is not covered with reducing hydrogen species at any time. It is further stated that glucose conversion to gluconic acid does not proceed under oxygen-free conditions; hence, oxygen is an essential compound in the reaction mechanism (Beltrame et al., 2006).

To clarify the situation for the gold catalyst used in the present study, analysis for both hydrogen peroxide and glucose conversion under oxygen-free conditions was carried out. As it can be taken from Figure 9 large amounts of hydrogen peroxide could be detected during the course of this reaction. Thus, the findings of Comotti et al. (2006c) are confirmed in this regard.

Glucose conversion to gluconic acid under oxygen-free conditions was carried out with a larger amount of catalyst (10000 mg l^{-1}) according to the procedure described in Section 2.7. If the reaction was carried out under otherwise standard reaction conditions, namely pH 9, only a very low glucose conversion (< 1 %) could be detected within 24 h. However, by adjusting a slightly higher pH value of 10.5, a considerable reaction rate could be achieved. During another 60 h, about 80 % glucose conversion was obtained. Analysis of the reaction mixture after this additional 60 h revealed that not only gluconic acid was produced to about 44 % of the total amount of formed products, but also hydrogenated products, mainly sorbitol, mannitol and xylitol, to about 28 % in the sum. The other products were the alkaline isomerisation products fructose and mannose (together 28 %), formed in a homogeneous reaction. No hydrogen peroxide formation could be detected during this experiment.

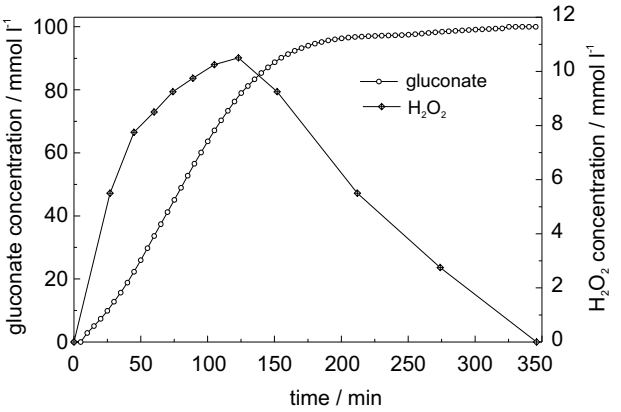

Figure 9:

Gluconate and hydrogen peroxide concentration versus time plot for a catalyst concentration of $c_{catalyst}$ = 200 mg l^{-1} at otherwise standard reaction conditions.

According to these findings, a mechanism for the gold catalysed glucose oxidation is most probable which is in between the classic oxidative dehydrogenation mechanism and the one suggested by Comotti et al. It seems reasonable to assume that the reaction starts with a nucleophilic attack of a hydroxide ion on glucose leading to a deprotonated geminal diol of glucose, which in the second step is likely to adsorb at the catalyst surface leading to electron-rich gold as shown in Figure 10. Thus far, the steps have already been suggested by Comotti et al. (2006c), who already pointed out that this pathway can easily explain reaction enhancement by alkali. Depending on whether or not oxygen is present in a sufficient amount, this adsorbed glucose species may react in two different ways.

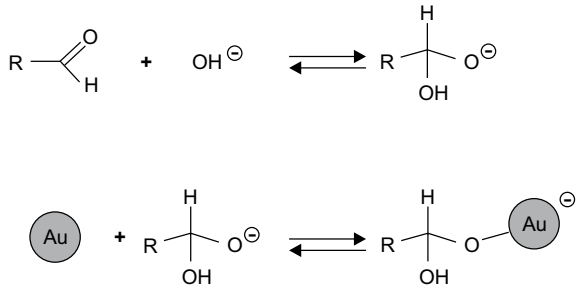

Figure 10:

Formation of the deprotonated geminal diol of glucose by nucleophilic attack of a hydroxide ion on glucose and adsorption of the formed glucose species at the gold surface

If no oxygen is present, the adsorbed glucose species is likely to decompose by hydrogen transfer to the catalyst surface as shown in Figure 11. This results in a desorbed gluconic acid species, which is further deprotonated to the gluconate anion under the alkaline reaction conditions, and hydrogen adsorbed at the catalyst surface, which is the source for the hydrogenated products observed under oxygen-free conditions in the present study.

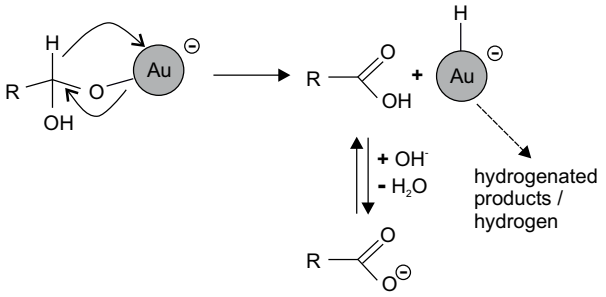

Figure 11:

Further reaction pathway of the adsorbed glucose species under oxygen-free conditions

If oxygen is present it will also adsorb at the catalyst surface according to the scheme shown in Figure 12. The linear oxygen adsorption, as well as oxygen and the glucose species being adsorbed simultaneously, have already been suggested by Comotti et al. (2006c). Their suggestion of an activated oxygen adsorption by the electron-rich gold surface likewise seems reasonable as adsorbed O_2^- species are favoured (Bond et al., 2006). However, from this state on, in our opinion, it seems to be more likely that the adsorbed glucose species will decompose in the same way as under oxygen-free conditions by hydrogen transfer to the gold surface. After gluconic acid desorption both a hydrogen species and the linear O_2^- species are co-adsorbed at the catalyst surface. Those two species will react in the final step to an adsorbed peroxide species which subsequently desorbs.

By this mechanism the formation of hydrogen peroxide and the formation of hydrogenated products can be explained. Oxygen is needed to clean the catalyst surface from adsorbed hydrogen. If oxygen is not present, or if oxygen adsorption is slow compared to glucose adsorption, hydrogenated products are produced.

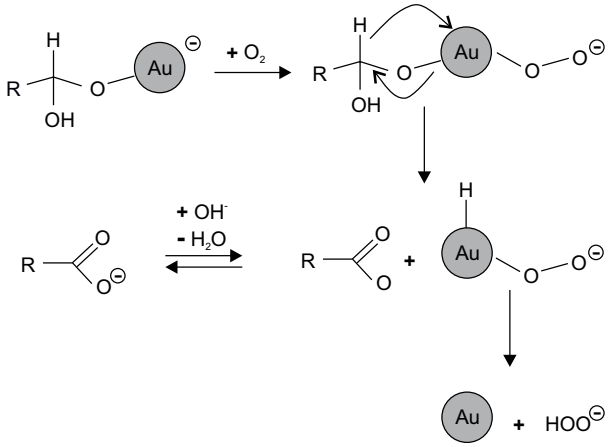

Figure 12:

Further reaction pathway of the adsorbed glucose species if oxygen is present

The main difference of the mechanism proposed here, and the classic oxidative dehydrogenation mechanism, is the fact that the gold catalyst adsorbs oxygen not dissociatively but in a linear manner. Linearly adsorbed oxygen results in peroxide species whereas dissociatively adsorbed oxygen would lead to water as product as it is formulated in the classic oxidative dehydrogenation mechanism proven for palladium and platinum based catalysts. This difference in oxygen chemisorption of the gold catalyst compared to palladium and platinum catalysts might also be the reason for the unusual high selectivity of gold in carbohydrate oxidation compared to palladium and platinum.

4. Conclusions

The kinetics of the liquid-phase glucose oxidation to gluconic acid has been investigated using a 0.3 % Au/Al_2O_3 catalyst prepared by the incipient wetness method. Oxygen mass transfer limitations were found to influence the catalytic activity below 50 % dissolved oxygen with regard to its saturation level. An increasing activity was found with increasing pH value in the range between pH 7 and 10 and with increasing temperature in the range between 20 and 60 °C, whereas the selectivity to gluconic acid remained unchanged at > 99 % under these conditions. The activation energy was determined to be 53 kJ mol^{-1}.

Compared to other kinetic studies of the gold-catalyzed glucose oxidation (Beltrame et al., 2006; Önal et al., 2004), a broader initial glucose concentration range between 10

and 1000 mmol l^{-1} was investigated in the present study. Analysis of the reaction orders with regard to glucose and oxygen led to the conclusion that the Eley-Rideal model should be discarded for the gold-catalyzed glucose oxidation.

During glucose oxidation with oxygen, considerable amounts of hydrogen peroxide are formed. The gold catalyst is able to oxidise glucose to gluconic acid under oxygen-free conditions; considerable amounts of hydrogenated products are also formed under these conditions. Both observations can be explained by a modified oxidative dehydrogenation mechanism, in which hydrogen from the adsorbed sugar is transferred to the catalyst surface where it reacts with a co-adsorbed linear oxygen molecule leading to hydrogen peroxide.

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