The effect of bismuth on the selective oxidation of lactose on supported palladium catalysts*

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ABSTRACT

The selective oxidation of lactose by molecular oxygen has been studied in a batch reactor containing an aqueous slurry of 0.5 kmol m⁻³ reactant and 1.0 kg m⁻³ catalyst. The in situ Bi promotion of a commercial Pd-C catalyst resulted in 100% selectivity to sodium lactobionate up to conversions of 95% in the pH range 7-10 and at temperatures up to 333 K. Performing the reaction under such conditions that the oxygen transfer to the liquid phase was rate-controlling allowed the production of sodium lactobionate in high yields in ~1 h. A maximum initial reaction-rate of 0.47 mol kg⁻¹ s⁻¹ was found at a molar Bi to Pd ratio of 0.50-0.67. Fifteen batches of lactose were oxidized with the same charge of catalyst without significant loss in initial activity or selectivity. Such other aldoses as maltose, glucose, and galactose could be oxidized analogously with similar selectivities.

INTRODUCTION‡

The oxidation of α-lactose monohydrate with molecular oxygen to sodium lactobionate is shown in Fig 1. High yields of lactobionic acid or its salts may be obtained from lactose by electrochemical, microbiological, or homogeneous catalytic oxidation.

The electrolysis of a lactose solution buffered with CaCO₃ or NaHCO₃ and with catalytic amounts of Br₂, Br⁻, or BrO⁻ ions is well known¹⁻⁶, as illustrated by a number of patents on this subject⁷⁻¹¹. The electrochemical oxidation of lactose with an organic peroxide such as H₂O₂ and a catalytic amount of an iodine-containing compound was recently patented¹².

Various aerobic microorganisms, notably of the genus Pseudomonas, are able to

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‡ List of symbols: [LAC], initial concentration of lactose, kmol m⁻³; [LAC], concentration of lactose as determined by h.p.l.c., kmol m⁻³; [LBA], concentration of sodium lactobionate as determined by h.p.l.c., corrected for diluting and sampling, kmol m⁻³; [LBA], concentration of sodium lactobionate as determined by h.p.l.c., corrected for diluting and sampling, kmol m⁻³; [Pd-C], concentration of catalyst (dry), kg m⁻³; [Pd-C], concentration of catalyst (dry), kg m⁻³; X, conversion of lactose; S, selectivity for sodium lactobionate; Y, yield of sodium lactobionate; R°, initial rate of lactose disappearance, mol kg⁻¹ s⁻¹; L°, liquid volume, m⁻³; W, mass of catalyst, kg.

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oxidize lactose and maltose directly to the corresponding aldobionic acids\textsuperscript{13-18}. The reaction sequence consists of two steps: the enzyme lactose dehydrogenase catalyzes the oxidation of lactose to lactobiono-1,5-lactone, and the latter is hydrolysed by another enzyme, lactonase, to lactobionic acid\textsuperscript{19-20}. The main drawbacks of the biochemical route are: difficulties in the separation of the microorganisms, control of byproducts, and disposal of waste water. Up to now, such procedures have only been used for the oxidation of D-glucose to D-gluconic acid.

Homogeneous catalytic oxidations of aldoses with several metal ions as catalyst and O\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, halogens, or HNO\textsubscript{3} as oxidants, have been reported\textsuperscript{21}. The drawbacks are similar to those already mentioned for the biochemical route.

The heterogeneous, noble metal-catalyzed oxidation of aldoses to aldonic acids has been studied in detail\textsuperscript{22-26}, without mentioning lactose. Because in the similar oxidation of ethanol with \textsuperscript{16}O\textsubscript{2}, no \textsuperscript{16}O is incorporated in the product\textsuperscript{27}, the mechanism of the reaction is thought to be a dehydrogenation of the hemiacetal or the hydrated aldehyde, followed by oxidative removal of chemisorbed hydrogen, as described in a previous paper\textsuperscript{28}.

Despite a reasonable number of patents\textsuperscript{29-38}, supported noble-metal catalysts are not currently used for the oxidation of sugars with oxygen. Commercial application of such a catalytic oxidation process will depend on the price and performance (namely activity, selectivity, and stability) of the catalyst.

Several recent French patents have claimed the use of a bismuth-modified palladium-on-carbon catalyst for the oxidation of aldoses, including lactose, to aldonic acids\textsuperscript{39-40}.

The best results were obtained with a Bi-Pd–C catalyst made by impregnation of an aqueous slurry of Pd–C with bismuth subnitrate, dissolved in concentrated hydrochloric acid. This treatment was followed by neutralisation with aqueous sodium hydrogencarbonate (4 h, 313–323 K), reduction with aqueous formaldehyde (1 h, 358 K), filtration, and washing.

In an earlier British patent\textsuperscript{41} the best results were obtained with a Bi-Pd–C catalyst made by the impregnation of active carbon with bismuth hydroxide nitrate, dissolved in concentrated hydrochloric acid (6 h, 298 K). Thereafter, an aqueous solution of

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Fig. 1. Oxidation of lactose to sodium lactobionate by molecular oxygen.
palladium chloride was added, followed by alcalinification with sodium hydroxide solution, reduction with a solution of formaldehyde (1 h, 353 K), filtration, washing, and drying. In comparison with the performance of an unpromoted palladium-on-carbon catalyst, both of the Pd-Bi-C catalysts described showed higher activity, and better selectivity and stability. This promoter effect has not yet been explained.

This paper reports on the in situ bismuth promotion of a commercial palladium-on-carbon catalyst, resulting in an active catalyst for the oxidation of aldoses, and in particular of lactose to sodium lactobionate, with 100% selectivity.

EXPERIMENTAL

Catalyst. Batches of a commercial 5% Pd-on-activated carbon catalyst (Degussa E 196 R/W) as delivered by the manufacturer, were used throughout this study. The Pd-Bi-C catalysts were prepared by adding the required amount of Bi(NO₃)₃·5H₂O (Merck) to a slurry of the Pd-C catalyst and the reactant solution, so as to obtain the desired Bi to Pd ratio.

Equipment, procedure and conditions. — All experiments were performed in a stirred tank-reactor setup as shown in Fig. 2. The temperature of the reactor was kept constant [10] within 0.5 K. The pH was controlled by automatic titration with 5M NaOH [8]. The pressure was kept at 0.1 MPa by admitting water from the burette [13] to the oxygen supply-vessel [12]. The consumption of alkali and oxygen were recorded as a

![Diagram](image-url)
function of time. A measure for the amount of oxygen dissolved was obtained from an oxygen probe [4] (Ingold 533 sterilizable electrode), which displayed the percentage of the equivalent saturation pressure of \( \text{O}_2 \) dissolved in the slurry. The \( \text{O}_2 \) concentration in the slurry was kept at a level < 1% of the equilibrium concentration during reaction by regulating the stirrer speed. The reactant solution was saturated with \( \text{N}_2 \), by stirring at reaction temperature, before adding the catalyst and the promoter. The suspension was kept under nitrogen for 1800s at the desired pH. The reaction was then started by stopping the stirrer and \( \text{N}_2 \) flow, quickly evacuating the gas-circulation system, refilling it with \( \text{O}_2 \), and restarting the stirrer. A filter at the bottom of the reactor allowed removal of the aqueous solution, while maintaining the catalyst in the reactor. Hence, more than one batch of lactose solution could be oxidized by a single catalyst loading.

Samples (2 mL) of the mixture, taken with a syringe, were filtered and stored at \( \sim 278 \) K. The composition of the mixture was determined by h.p.l.c. as a function of time. Concentrations of sugar acids were determined as described by Dijkgraaf et al., using an eluent composition of 9.28 g NaCl and 4.2 g MgCl\(_2\)\cdot6H\(_2\)O per L. Concentrations of sugars were determined as described by Verhaar et al. The measured concentrations were corrected for the dilution with NaOH and for the effects of sampling.

Unless stated otherwise, the following set of standard reaction conditions was applied: pH 9, \( T \) 323 K, \( \Gamma \leq 1\% \), [lactose] 0.5 kmol m\(^{-3}\), [catalyst] 1.0 kg m\(^{-3}\), and a molar Bi to Pd ratio of 0.50. The conversion of lactose, \( X \), the selectivity, \( S \), and the yield of sodium lactobionate, \( Y \), were defined as:

\[
X = 1 - \frac{[\text{LAC}]}{[\text{LAC}]_0} \quad (1)
\]
\[
S = \frac{[\text{LBA}]}{([\text{LAC}]_0 - [\text{LAC}])} \quad (2)
\]
\[
Y = XS = \frac{[\text{LBA}]}{[\text{LAC}]_0} \quad (3)
\]

Initial rates of lactose disappearance were obtained from the continuity equation for lactose:

\[
R^o = \frac{V [\text{LAC}]_0}{W} \frac{dX}{dt} \bigg|_{t = 0} \quad (4)
\]

At 100% selectivity for sodium lactobionate, \( R^o \) equals the rate of the oxidation reaction shown in Fig. 1 and is proportional to the feed rate of alkali, which is added to maintain a constant pH. It should be stressed that the rates reported in this paper are controlled by the transfer of \( \text{O}_2 \) from the gas to the liquid phase.

RESULTS AND DISCUSSION

Balances. — Figure 3 shows the results of a typical experiment in which the alkali consumption, the \( \text{O}_2 \) consumption, the concentrations of lactose \([\text{LAC}]\), sodium lactobionate \([\text{LBA}]\) and the carbon balance expressed as the sum of \([\text{LAC}]\) and \([\text{LBA}]\) were recorded as a function of time. The alkali consumption matches the production of
sodium lactobionate and equals twice the $O_2$ consumption. The carbon balance is satisfied within experimental error.

**Effect of the Bi to Pd ratio on the selectivity.** — Figure 4 shows the selectivity for sodium lactobionate as a function of conversion for the Bi-Pd–C (molar Bi to Pd ratio is 0.50) and Pd–C-catalyzed oxidation of lactose. Fig. 4 demonstrates that 100% selectivity and correspondingly high yields are maintained up to 95% of conversion for the Bi-Pd–C catalyzed reaction. No side products were detected by h.p.l.c. Similar results were obtained for the oxidation of $D$-maltose, $D$-glucose, and $D$-galactose.

At low conversions, no influence of the Bi to Pd molar ratio was detected on the selectivity for sodium lactobionate. The Bi-Pd–C-catalyzed oxidation (molar Bi to Pd ratio is 0.50) showed a 100% selectivity, even at conversions >80%, where the selectivity of the unpromoted Pd–C-catalyzed oxidation decreased.

**Effect of the Bi to Pd ratio on the initial reaction rate.** — The initial reaction rate, $R^0$, was measured for various Bi to Pd molar ratios at standard reaction conditions, as shown in Fig. 5. Figure 5 clearly demonstrates the promoting effect on $R^0$ when a Bi salt is added to the Pd–C catalyst in the reaction mixture. Compared with the oxidation procedure using the standard Pd–C catalyst, initial reaction rates are 2–3 times as high. The maximum initial reaction rate amounted to 0.47 mol kg$^{-1}$ cat. s$^{-1}$ and was obtained at a molar Bi to Pd ratio of 0.50–0.67. At higher Bi to Pd ratios, the initial rate decreases to a level lower than that of the unpromoted Pd–C-catalyzed oxidation. The observed effects would be even more pronounced in the absence of $O_2$-transfer limitations.

**Effect of time on stream on the reaction rate.** — The experimental reaction setup
allowed operation only in the batch mode, which resulted in non-steady concentrations, as shown in Fig. 3. The curves shown in Fig. 3, in particular their slopes, are determined by the rate of oxidation. The latter depends not only on the process variables, such as temperature, concentration, and the initial catalyst activity, $R_0$, expressed as the initial rate of oxidation, but also on the catalyst stability during reaction.

Catalyst deactivation caused by $O_2$ during reaction has been reported in the literature. The data presented in Fig. 3 do not allow assessment of the importance of catalyst deactivation. A continuous-reactor setup would be required to do so. It was possible, however, to compare the initial activities and selectivities obtained on a single catalyst charge after oxidation of several batches of lactose. After nearly complete conversion of the reactant, the mixture was removed under nitrogen. The catalyst was then washed with 250 mL of distilled water, and filtered again. A fresh lactose solution was introduced into the reactor, and the standard-start procedure was used.

In this way, 15 batches of lactose were oxidized by the same charge of Pd-Bi-C catalyst without any significant loss in initial activity and selectivity. It turned out to be crucial for the activity of the catalyst to pay special attention to the oxygen concentration in the reaction slurry. If the partial oxygen pressure was not controlled in the way described, the Pd-Bi-C catalyst was deactivated.

Effect of pH and temperature on selectivity. — The selectivity for sodium lactobionate at a conversion of 80% was determined in the pH range 6–11 and at a temperature of 323 K. No reaction was noted below pH 7. A 100% selectivity for sodium lactobionate was found in the pH range 7–10. At pH > 10, alkaline degradation
influence of the molar Bi to Pd ratio on the maximum initial reaction rate for the Pd-Bi-C-catalyzed oxidation of lactose to sodium lactobionate. Reaction conditions: pH 9, T 323 K, \( r < 1\% \), [LAC] 0.5 kmol m\(^{-3}\), [catalyst] 1.0 kg m\(^{-3}\).

Of lactose occurred, as reflected in the appearance of a yellow-brown color and a decrease of selectivity.

The selectivity for sodium lactobionate at a conversion of 80% was also determined in the temperature range 303–343 K and at pH 9. The 100% selectivity for sodium lactobionate decreased at temperatures > 333 K probably because of the enhancement of undesired side-reactions. The French and British patents\(^{39-41}\) report similar effects of pH and temperature.

CONCLUSIONS

A rapid and easy method is described for the *in situ* bismuth promotion of a Pd–C catalyst, resulting in an active catalyst for the oxidation of aldoses, in particular lactose. A maximum initial oxidation rate for lactose of 0.47 mol kg\(^{-1}\) s\(^{-1}\) was found at a molar Bi to Pd ratio of 0.50–0.67. Promotion by Bi allows lactose to be oxidized to sodium lactobionate with 100% selectivity in the pH range 7–10 and at temperatures up to 333 K.

Performing the oxidation of 0.5 kmol m\(^{-3}\) lactose with 1.0 kg m\(^{-3}\) Bi-Pd–C under conditions where oxygen transfer from the gas to the liquid phase is rate-controlling affords yields of 95% of sodium lactobionate in \( \sim 1\) h, the carbon balance being within experimental error. Other aldoses such as D-maltose, D-glucose, and D-galactose may be oxidized comparably, with similar selectivities.
ACKNOWLEDGMENT

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