Highly Selective Oxidation of Lactose to Lactobionic Acid over Low-Loading Pd-Bi/SBA-15 Catalyst under Microaerial Conditions

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Introduction

Lactose, a milk sugar, is a major component of whey, the main by-product in cheese and casein production. Lactose surplus estimate is about 1.2 million tons/year worldwide [1]. Only a small percentage of that amount is utilized further. The remaining, if disposed off in the waste streams can create environmental problems due to its high biological oxygen demand. With tighter environmental regulations and restrictions, new routes for further utilization of lactose have to be explored. Lactose is useful for food and pharmaceutical applications and provides an interesting starting material for the synthesis of value-added carbohydrates and derivatives. Very little progress has been made in lactose utilization technologies. Lactobionic acid, 4-β-(galactosido)-D-gluconic acid obtained by lactose oxidation is comprised of one molecule of galactose attached to one molecule of gluconic acid via an ether-like linkage. Lactobionic acid (LBA) exhibits interesting chelating properties [2]. It is a potent ingredient for the preservation of organs during transportation [3]. Also, it represents a new ingredient in skin care products featuring potent antioxidant and humectant properties [4].

The aim of this work is to selectively produce LBA for use in both therapeutic and pharmaceutical applications via the partial oxidation of lactose over novel very low metal loadings active and stable Pd-catalysts with Bi as promoter supported on mesoporous silica SBA-15 material under microaerial oxidation conditions..

Materials and Methods

Hexagonally ordered SBA-15 was synthesized in acidic medium via a synthetic route using triblock copolymer (Pluronic 123) as a templating agent. Bi-Pd/SBA-15 catalysts were prepared by successive impregnations of calcined SBA-15 with aqueous solutions of metals ($Pd(NO_3)_2.xH_2O$ and $Bi(NO_3)_2.5H_2O$), followed by drying at room temperature for 24 h, calcination in air at 540 °C for 5h, and reduction under hydrogen flow at 400 °C for 3h and at 260 °C for 2 h for the first and second impregnations, respectively. Various catalyst loadings and Bi/Pd ratios were investigated. The catalysts were characterized using different techniques.

Lactose oxidation experiments were performed in aqueous phase using a solution volume of 100 mL and predetermined amount of pre-reduced catalysts in a thermostated and magnetically stirred 300 mL-glass reactor at atmospheric pressure under controlled pH and maintained microaerial conditions (<1% of dissolved O_2 equilibrium concentration at reaction temperature, i.e. ≈ 1 μM) throughout the reaction duration. Three aeration procedures were investigated to insure microaerial conditions. The reactants and products were analyzed by HPLC (ICS 2500 from Dionex).

Results and Discussion

Table 1 summarizes the obtained conversion and selectivity towards LBA under different operating conditions. In terms of catalyst formulation, bimetallic catalysts proved to be more active than Pd-monometallic counterpart. Optimal formulations were 1.02-0.64 wt% Pd-Bi corresponding to a molar ratio Bi/Pd of 0.3. Furthermore, Table 1 allows concluding that for the same catalyst formulation, the higher the ratio catalyst to lactose, the higher the lactose conversion even though selectivity to LBA decreased slightly.

Table 1 Performances of different formulated Bi-Pd/SBA-15 catalysts for partial oxidation of lactose (21 mM) to lactobionic acid in aqueous solutions at 65 °C, pH 9 after 3 h of reaction.

Aeration procedure	Pd (% wt)	Bi (% wt)	Cata/Lact (g/g)	Conversion (%)	Selectivity (%)
1	1.00	0.00	0.14	36.14	92.63
1	5.00	5.00	0.14	46.84	87.63
1	1.07	1.08	0.14	60.48	80.62
1	1.02	0.64	0.14	67.88	86.36
1	0.81	0.44	0.14	62.20	95.93
1	0.83	0.82	0.14	53.35	94.17
1	0.50	0.50	0.14	18.45	92.14
2	1.02	0.64	0.14	77.62	100.00
2	1.02	0.64	0. 21	83.58	93.67
2	1.02	0.64	0.28	89.64	87.49
2	0.81	0.44	0.28	95.01	100.00
3	1.02	0.64	0.14	82.54	84.23
3	1.02	0.64	0. 21	96.14	100.00
3	1.01	0.22	0.14	66.24	100.00

Within the conditions investigated, the catalyst was very active and demonstrated a perfect selectivity towards the formation of LBA. Furthermore, it exhibited a pretty good stability towards metal leaching. Controlling the amount of dissolved oxygen in the reaction mixture under microaerial conditions is the best way for conducting the oxidation of lactose at the highest conversion and selectivity towards LBA formation.

Significance

The industrial significance of the present work relies on the high selectivity of the bimetallic catalyst thus avoiding tedious and costly separation operations as well as the very low noble metal loading of the formulated catalysts thus lowering the catalyst costs.

References

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