

Selective Liquid-phase Oxidation of Lactose to Lactobionic Acid

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Introduction

Lactose (LA) is a major component of whey, the main by-product in cheese production in dairy industry. Cheese whey typically contains about 5 wt. % lactose, which can be converted to lactobionic acid (LBA) by selective oxidation. This acid has antioxidant properties and its largest commercial use is as an important constituent to preserve solutions for human organs during transplantation procedures. LBA is also employed as acidulant, complexing agent and antioxidant in food and pharmaceuticals. Nowadays, LBA is produced by microbiological oxidation of LA. The main disadvantages of this process are the long times required to achieve high levels of conversion and the formation of hydrogen peroxide as a byproduct [1]. Recently, there has been increasing interest in the LBA production by heterogeneous catalytic oxidation of LA. Some authors have studied LA oxidation using different metals and supports [2,3]. It was found that metal, pH, temperature and O₂ concentration has important influence on this reaction. The aim of this work is to analyze the effect of support, metal and initial lactose concentration in the liquid-phase LA oxidation at low temperature (65°C) and pH= 9 in order to obtain high yield and selectivity to LBA.

Materials and Methods

Calcined SiO₂ (Sigma-Aldrich) and Al₂O₃ (CK-300 Cynamid Ketjen) were used as supports. H₄PtCl₆ (Sigma-Aldrich) and HAuCl₄ (Sigma-Aldrich) were the metal precursors. Pt-based catalysts were prepared by incipient wetness impregnation and Au-based catalysts by precipitation-deposition method. Samples were then calcined at 500°C in air flow. Pt/SiO₂ and Pt/Al₂O₃ were reduced in H₂ flow at 300°C. All samples had a 2 wt. % metal content. Catalysts were characterized by N₂ physisorption at -196°C, XRD, H₂ chemisorption and STEM. Catalytic experiments were performed in a thermostated (65°C) and stirred (1000 rpm) 300 mL-glass reactor. Initial lactose concentration was varied between 0.03 and 0.18 M. The pH was kept constant at 9 during reaction by controlled addition of a 1 N NaOH aqueous solution. The system was equilibrated at 65°C and O₂ was fed by air bubbling. Samples at different reaction times were taken and analyzed by HPLC, using a Phenomenex (Phenosphere 5 micras, NH₂, 80Å, 250mm x 4.60 mm) column and a Shimadzu RID-10A refractive index detector.

Results and Discussion

Specific surface area, pore volume and pore diameter of samples were similar to those of support, indicating that metal incorporation did not affect support textural properties. X-ray diffractograms did not show crystalline phases of metallic Pt or Au indicating that these metals were probably highly dispersed over the support. Metallic dispersion, measured by H₂ chemisorption, was 10% for Pt/SiO₂ and 30% for Pt/Al₂O₃ so the mean particle size was between 10 and 5 nm. Au/Al₂O₃ sample was analyzed by STEM: a narrow particle distribution in the range of 2-7 nm, with a 3.7 nm average particle diameter was determined (Fig. 1).

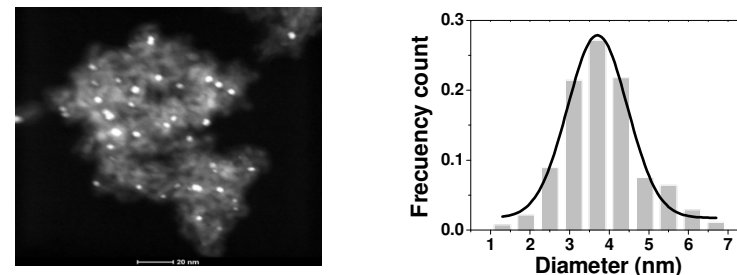


Figure 1. STEM of Au(2 wt. %)/Al₂O₃ (left) and metal particle size distribution (right)

Oxidation experiments over Pt/SiO₂, Pt/Al₂O₃ and Au/Al₂O₃ with an initial LA concentration of 0.12 M showed that, after 180 min, the LA conversion over Pt/SiO₂ was only about 9%, while for Pt/Al₂O₃ was 23%. This activity difference could be assigned to the mayor dispersion of metallic Pt over Al₂O₃ compared with SiO₂. Furthermore, Au/Al₂O₃ was much more active than Pt/Al₂O₃: 85% LA conversion was achieved after 180 min. In all cases, for the conditions used in this work, the only oxidation product detected was LBA.

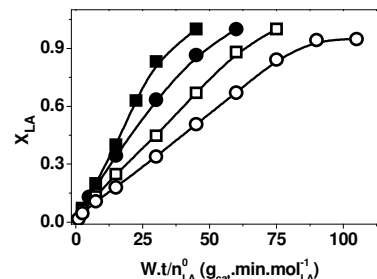


Figure 2. Lactose conversion (X_{LA}) as a function of reaction time for different initial lactose concentration: (■) 0.03 M (●) 0.06 M (□) 0.12 M (○) 0.18 M

Experiments with different initial LA concentration, between 0.03 and 0.18 M were carried out with Au/Al₂O₃ in order to estimate the reaction order respect to LA. It was determined that, for a given reaction time, the LA conversion decreased as the initial concentration was raised (Fig. 2). This trend indicates that LA is strongly adsorbed on the metallic Au surface. A reaction order respect to LA of -0.5 was estimated by applying linear regression. On the other hand, it was determined that Au/Al₂O₃ activity was kept constant after two consecutive runs, indicating a good stability of this catalyst under the reaction conditions used in this work.

Significance

Total lactose conversion with 100% selectivity to lactobionic acid was obtained using a highly dispersed and stable Au(2 wt. %)/Al₂O₃ catalyst.

References

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