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ONE-POT GOLD-CATALYZED OXIDATIVE MODIFICATION OF FREE SUGARS UNDER OXYGEN FOR THE SYNTHESIS OF BIOBASED HIGH ADDED VALUE PRODUCTS

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PURPOSE OF THE ABSTRACT

Thanks to the abundance and renewability of sugars, carbohydrate-based products are an excellent alternative to petrosourced products from a sustainable point of view. [1] They find applications in various fields such as pharmaceuticals, cosmetics, detergents, etc. [2] Nevertheless, carbohydrates are polyfunctional compounds and usually, their modification by conventional glycochemistry doesn't meet the green chemistry principles [3] and shows difficulties to be transferred to industrial scales: ie. multi-step protocols, energy/time consuming steps, hazardous chemicals are often required. In addition, cost of production of sugar-based compounds can hamper their use in industrial fields where petrochemical substances remain more competitive (detergency for instance). Development of greener and more economic approaches, that allow modifying selectively free carbohydrates represent therefore an important stake. In particular, heterogeneous catalysis is one of the pillars of sustainable chemistry improving the eco-efficiency of a synthetic strategy.

Due to their unique physical, optical and chemical properties, gold nanoparticles (Au NPs) raised particular consideration in various fields such as sensing, medicine, catalysis etc. Particularly, the aerobic gold-catalyzed oxidation of alcohols and sugars has been widely investigated. [4] From an eco-conception point of view, this approach shows many advantages: (i) the reaction is generally performed in water, (ii) O2 is used as oxidant, (iii) gold is biocompatible, non-toxic and much less expensive than other metals such as Rh, Pd and Pt, (iv) Au NPs can be supported onto an insoluble material easily recycled, and (v) the catalyst is generally synthesized following mild and cheap procedures. We recently described an efficient and versatile method for selective oxidation of sugars into corresponding sodium aldonates. Using hydrogen peroxide as cheap and green oxidant, and 0.004 mol % of gold in basic conditions, a quantitative and selective oxidation of aldoses was achieved in 10 to 20 min depending on the activation mode (MW or illumination). [5,6]

We now focus our research on the one-pot synthesis of sugars derivatives via lactones or ester platform molecules in situ formed. Conventionally, the modification of carbohydrates into aldonic esters or lactones requires a two-step procedure: a first oxidation followed by an esterification or lactonization step. With this new procedure, free sugars were functionalized through a one-pot oxidation/lactonization reaction in mild conditions using Au/CeO2 as catalyst (figure 1). The reaction was achieved in less than 4h with only 0.18 mol % of gold in the presence of oxygen. A mixture lactone/methylester is completely and selectively obtained starting from the

aldose. This crude can then quantitatively react with an amine in less than 1h, leading only to the corresponding aldonamide following a 1 pot/2 steps procedure (oxidative amidation). In this communication, we will describe the nanocatalyst synthesis and its characterization, and discuss the optimization of the experimental parameters leading to oxidation/lactonization. The results obtained on the oxidative lactonization and/or amidation of a variety of sugars will be discussed. Finally, we will bring some insights on the supposed mechanism of this one-pot oxidative procedure, in particular based on ESR spectroscopy.

FIGURES

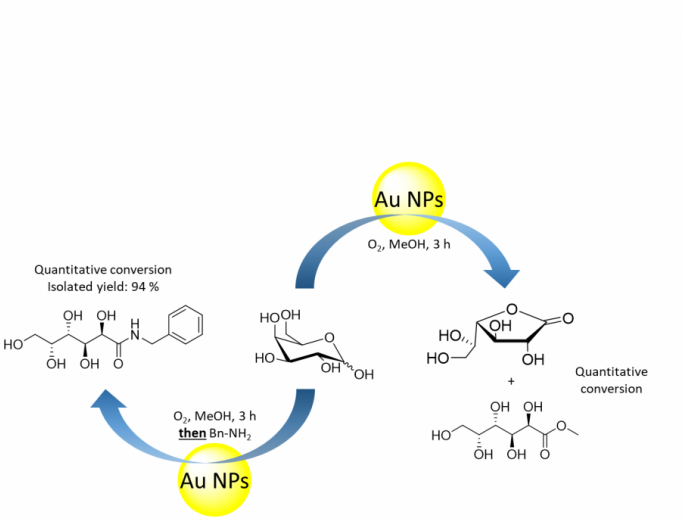

FIGURE 1

FIGURE 2

Figure 1

One-pot oxidation/lactonization and oxidation/amidation of D-galactose used as model

KEYWORDS

free carbohydrates | gold catalysis | one-pot oxidative lactonization | one-pot/2-step oxidative amidation

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