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Glucose oxidation using supported gold catalysts: experimental and computational studies for elucidating reaction mechanism and deactivation phenomena

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PURPOSE OF THE ABSTRACT

Heterogeneous catalysts have been playing a fundamental role in recent years for the enhancement of biomass. They have in fact made possible to make numerous processes more productive and sustainable, thanks to the possibility of regeneration. Depending on the material used, it is possible to catalyze numerous reactions, converting the biomass into building block chemicals of high industrial interest. However, it should be noted that there are some limitations in the reusability of a catalyst, for example for deactivation phenomena. In particular, we focused on understanding the causes of deactivation of the catalysts used in the laboratory in the reaction of oxidation of glucose (GLU) to glucaric acid (GLA) in liquid phase using supported gold nanoparticles. Indeed, GLA has been identified as a top value-added chemical from biomass [1] that can be employed for many uses: for instance, it could be a precursor of adipic acid, a monomer of Nylon-6,6. GLA can be synthetized by the oxidation of GLU, passing through the intermediate gluconic acid (GLO), as reported in Figure 1.

In recent years, a new process has been developed to obtain GLA in an economic and environmentally sustainable way, in order to replace the current use of HNO3 as a stoichiometric oxidant, or electrocatalysis and biochemical synthesis, which show several disadvantages. In particular, this process is focused on the use of catalysts based on gold nanoparticles supported on activated carbon or metal oxides for the oxidation reaction of GLU to GLA using O2 as an oxidant agent in presence of NaOH as a base.

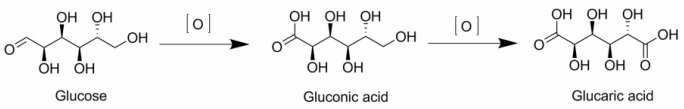
We observed that during the reaction the GLA yield reached a plateau and indicating a possible catalyst deactivation due to GLA or other byproducts. To elucidate the cause of deactivation it was decided to carry out computational studies, analyzing the adsorption energies of the main molecules involved in the reaction, in order to understand which intermediate or product could be the one that leads to the deactivation of the catalyst.

DFT studies were then carried out, using the Gaussian 16 software. For glucose oxidation, a ?cluster approach? was used: we modeled three types of Au55 clusters, i.e. amorphous [2] and symmetric ones [3], that model distorted surfaces in realistic small particles (of ca. 1 nm) and the Au(100) and Au(111) surface clusters [4] that model extended surfaces on larger nanoparticles.

Results show that amorphous structures are much more stable than the symmetric icosahedral (ICO) and the cubo-octahedral (CUBO) ones, due to relativistic effects. We then proceeded to study the adsorption of different molecules on all these structures: OH-, GLU, GLO and GLA. As regards the adsorption of OH-, it has been seen that this tends to preferentially position itself in a bridge position on both exposed surfaces. On the nanoparticulate structures, on the other hand, it is positioned in bridge or in top depending on the coordination of

the chosen gold atom, but it is still more stable in the bridge position. Regarding the study of the adsorption of GLU, GLO and GLA, it has been seen that GLA is the one that, on the amorphous Au55 structures, it tends to adsorb itself more strongly, in agreement with the experimental data. Theoretical studies were also performed on the effect of the basic environment, evaluating the interactions between the OH- groups adsorbed on the surfaces of the catalyst and the three molecules under study.

FIGURES



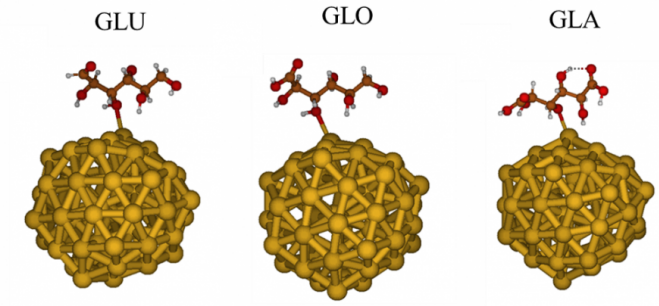


FIGURE 1

Glucose oxidation pathway towards glucaric acid via gluconic acid

[o]: oxidation

FIGURE 2

GLU, GLO and GLA adsorption on Au55 clusters

GLU: glucose

GLO: gluconic acid

GLA: glucaric acid

KEYWORDS

computational modeling | green chemistry | glucose oxidation | gold supported nanoparticles

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