

Electronic Effect of Polymeric Stabilisers on the Catalytic Activity of Supported Au Nanoparticles for the Selective Oxidation of HMF

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Abstract

It is widely documented that the catalytic activity of supported metal nanoparticles (NPs) is correlated to their size and shape,¹ consequently, stabilising molecules are usually employed during their preparation to control these properties. However, these capping agents can significantly affect catalytic activity. Indeed, the accessibility to active sites can be partially blocked by the polymer, and the stabiliser steric and electronic properties can influence the reaction mechanism. Therefore, the complete understanding of NPs stabiliser role is becoming more and more important for catalyst design. Several works have shown how removing the stabiliser influences the catalytic performances, but only few have paid attention to the effect that these molecules have on the catalytic properties.

In our previous work², we have shown how different stabilising agents can affect Au-NPs activity in the selective oxidation of 5-hydroxymethyl-furfural (HMF) to produce 2,5-furandicarboxylic acid (FDCA), modifying their dimensions and gold exposure.

The main purpose of this work was to study the effect of the charge transfer caused by the electronic properties of polymeric stabilisers on Au nanoparticles activity, using HMF oxidation as a model reaction. In particular, a series of gold-based catalysts prepared via sol-immobilization and supported on active carbon, (Au/AC) were tested. To study the influence of different stabiliser electronic properties on catalytic performances, two polymers with different functional groups, poly-vinyl alcohol (PVA) and poly-vinylamine (PVAm), and a series of copolymers PVA-co-PVAm, with different PVA/PVAm ratio, were synthesised and employed as NPs stabilisers. In fact, these polymers have similar structures, but the amino group is a stronger electron-donor than the hydroxyl group, thus the charge transfer between the stabilizer groups and the metal surfaces is different. A study on the reaction intermediates has demonstrated that a different reaction mechanism, already observed on calcined Pd-Au bimetallic nanoparticles,³ takes place on the PVAm-stabilised catalyst. The strong electron-donor nature of the poly-vinylamine affects the catalyst properties, leading to a dramatic change in the NPs activity, altering the reaction mechanism. The gold NPs are partially charged by the stabiliser and their role of electron-acceptor is inhibited. However, decreasing the number of electron-donor groups, it was possible to observe a variation of the reaction mechanism and an improvement in the catalytic performances. This study highlighted the importance of considering the stabiliser presence during the catalyst design.

References

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