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Stabiliser's effect on Au nanoparticles activity for the selective oxidation of HMF

AUTHORS

Alessandro ALLEGRI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Francesca LIUZZI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Stefano SCURTI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Daniele CARETTI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Nikolaos DIMITRATOS / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Stefania ALBONETTI / DEPARTMENT OF INDUSTRIAL CHEMISTRY - UNIVERSITY OF BOLOGNA, VIALE DEL RISORGIMENTO 4, BOLOGNA
Corresponding author : Stefania ALBONETTI / stefania.albonetti@unibo.it

PURPOSE OF THE ABSTRACT

Nowadays, nanostructured materials are employed in several fields such as medicine, biology, and chemistry. In particular, the role of nanoparticles (NPs) in heterogeneous catalysis has attracted a significant interest: supported metal nanoparticles have been found to be very active for a great assortment of reactions. It is widely documented that the activity of these catalysts is correlated to the size and shape of NPs,[1] consequently, stabilising molecules are usually employed during the preparation of the catalysts. The active sites of the catalysts can be partially or entirely blocked by the stabiliser molecules decreasing the overall detected activity, but steric and electronic effects of the stabilisers can also improve the catalytic performances.[2] For this reason, the role of the nanoparticles stabilisers is becoming more and more important during catalyst design. Several works have shown how removing the stabiliser influences the catalytic performances,[3] but only few have paid attention to the effect that these molecules have on the catalytic properties.[4]

On these bases, the main purpose of this work was to study the effect of some polymeric stabilisers on the activity of gold nanoparticles, using 5-HydroxyMethylFurfural (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 in the selective oxidation of HMF to produce 2,5-FuranDiCarboxylic Acid (FDCA).

Results and discussion

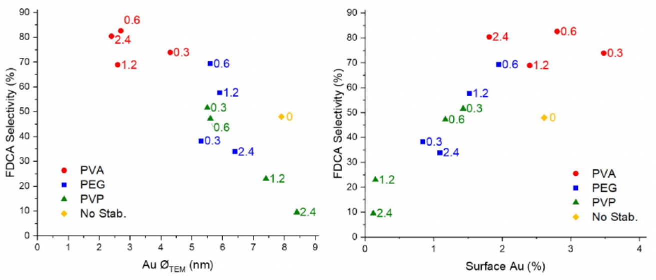
Firstly, three commercial polymers (PVP, PEG and PVA) were employed as NPs stabilisers to synthesise three series of Au/AC catalysts. For each series of catalysts, the polymer/Au weight ratio was varied from 0.3 to 2.4 to study how the stabiliser amount can affect the catalytic performances. All the catalysts were tested in the HMF oxidation, and the results were compared with the characteristics of the catalysts to better understand how the polymer affects the catalytic performances. In particular, the NPs dimensions and Au exposure on the catalysts surface were measured through TEM and XPS analysis, and the comparison between these features and the catalytic performances has highlighted some interesting results (Figure 1). FDCA selectivity is well correlated with the NPs size and the gold surface exposure, which are influenced by the stabiliser's presence. Higher amounts of

PVA further decreased the average diameter of Au nanoparticles, but decreased the percentage of gold surface, while at higher amount of PVP and PEG stabilisers, a significant increase of the mean Au particle size, as well as a decrease in the gold surface exposure, was observed.

Since PVA-stabilised catalysts have shown better performances, a similar polymer, polyvinyl amine (PVAm), with a different functional group (-NH2), has been synthesised, in order to study how different electronic properties of the stabilising agent can affect the catalyst activity. Nanoparticles stabilised with PVAm have shown similar TEM dimension to those stabilised with PVA. A study on the reaction time was performed on the Au/AC_PVAm and Au/AC_PVA catalysts with a 0.6 polymer/Au weight ratio (Figure 2). Interesting results emerge from this study: the evolution of the products distribution during the reaction time is completely different between the two catalysts. A different reaction mechanism, already observed on certain Pd-Au bimetallic nanoparticles,[5] takes place on the amine-stabilised catalyst. The strong electron-donor nature of the polyvinyl amine affects the catalyst properties, leading to a dramatic change in the Au NPs activity, altering the reaction mechanism.

These studies highlighted a double effect of the capping ligand: its presence leads to smaller and more active nanoparticles, but, at the same time, its presence might hinder catalytic activity either via steric or electronic phenomena.

FIGURES



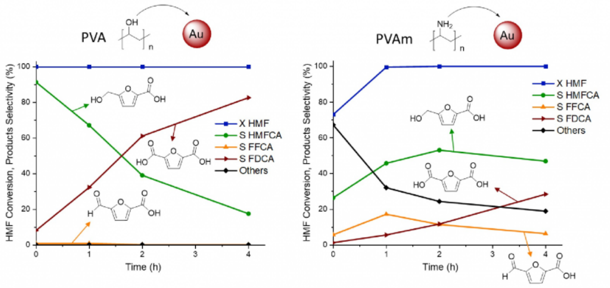


FIGURE 1

Figure 1

Correlation between catalytic performances and particles size (Left) and between catalytic performances and surface Au% (Right) for different catalysts. For each catalyst, the polymer/Au weight ratio is reported .

FIGURE 2

Figure 2

Comparison between the reaction time studies for the Au/AC_PVA (Left) and Au/AC_PVAm (Right) catalysts.

KEYWORDS

Gold nanoparticles | Stabilising agent | HMF oxidation | Reaction mechanism

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