

DFT models for first step of the Chemoselective Hydrogenation of Substituted Aldehydes Using Silver Nanoparticles as Catalyst

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Piet van Leeuwen recently published [1,2] studies about Au nanoparticles stabilized by secondary phosphine oxides (SPOs) and its use as catalyst for the hydrogenation of substituted aldehydes. Silver compounds have desirable physical properties, good relative abundance and low cost; however, there are only a few studies describing its properties. Bigioni et al. published [3] the crystallographic results to $M_4^+[Ag_{44}(p-MBA)_{30}]^4$ (where M_4^+ = alkali counterions and p-MBA = p-mercaptobenzoic acid), which has a very stable Ag₃₂ core. Similarly, Bakr at al. published [4] a reversible size control of Silver nanoparticles via ligand-exchange, in which, they observed the metal-ligand binding energy has huge importance in the size of the nanoparticle.

This work aims to understand the interaction of Silver nanoparticles with SPOs starting from complexes of this metal to describe the nature of the interactions between them and describe also the heterolytic cleavage process of hydrogen with complexes of this metal (from step 1 to step 2 in Figure 1). It was done by theoretical studies of the first step of the mechanism proposed by van Leeuwen to the hydrogenization of substituted aldehydes [1] [2] using Ag instead of Au as the metal in nanoparticle. Two models were studied: i) Ag₁-SPOs complexes; ii) Ag₃₂-SPOs nanoparticles. The geometries both complexes and nanoparticles, except the Ag₃₂ core, were full optimized using the Orca package was made in our previous work [5] to chalcogenate-protected gold nanoclusters.

In model (i), two approximations were tested. The H₂ going towards O (step 3) and the H₂ going towards Ag (step 4) where the last one is more stable by 2.3 kcal/mol. The reaction paths from these initial approximations (steps 3 and 4) to products (step 2) produced two transition states (steps 32_TS and 42_TS) where the first one is about 17.2 kcal/mol more stable than the last one. All ground states (steps from 1 to 4) have no imaginary frequencies or have only a few of them below 20 cm⁻¹. The transition state 32_TS has one imaginary frequency at 1210.17 cm⁻¹ and the 42_TS has one in 605.83 cm⁻¹. As the product is (step 2), we believe there is a reaction path from 42_TS to 32_TS as showed in Figure 2. From our results we concluded that the reaction starts with the H₂ going towards Ag (step 4), following by steps 42_TS, 32_TS and reach the product (step 2).

In order to evaluate how far is model (i) from model (ii) we compare the Ag_1 -(SPO)₂ with the Ag_{32} -(SPO)₂ (Figure 3). The geometries are quite similar, except for the



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bond Ag-P which is longer in Ag₃₂-(SPO)₂, in this way, model (i) seems to be good enough to model the nanoparticle reaction path.



Figure 1. Models steps of the H_2 approximation of the nanoparticle. Steps (1), (2), (3) and (4) are ground states and steps (32_TS) and (42_TS) are transition states.



Figure 2. Reaction path proposed to the first step.

Key-words: **SPO**, nanoparticles, hydrogenization, silver.

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