

# [Hakkinen oxygen-assisted selective dehydrogenation of the biomassderivedlignan hy...](https://assignbuster.com/hakkinen-oxygen-assisted-selective-dehydrogenation-of-the-biomassderivedlignan-hydroxymatairesinol/)

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Hakkinen et al.

34 individuated three main factors that could rule the reactivity of supportedsubnanometric clusters: electronic characteristics, cluster fluxionality (i. e. cluster reconstructioncaused by the presence of defects or adsorbates), dopants and impurities.

Actually, the latter could be, in a more or less direct way, also related to the electronic e? ects asclearly explained by Campbell et al. 35 in a revisitation of the well known Strong Metal SupportInteraction (SMSI) e? ects. It should be stressed that these e? ects could assume muchmore importance in the subnanometric regime since, for cluster of 6-10 atoms, the numberof atoms directly in contact with the support could be a significant fraction of the total. Consequently, multiple processes involving metal-support interactions can contribute to theoverall properties of the catalysts. In a pretty recent letter of Ahmadi et al. 36, they proposedthe following list of important e? ects exerted by the support:• charge transfer from the support (or viceversa);• perimeter activation and synergistic interactions.

Due to their di? erent environment, metallic atoms at the support interface could show di? erent reactivity. Moreover, vicinal support atoms could contribute to the reaction progress, providing adsorptionsites for the reactants;• structural changes in the subnanoparticle. Geometry of isolated and supported metallicclusters may significantly vary. In a more general view, metal-support interactions maycontribute to rule shapes and sizes of the supported clusters, controlling nucleation andgrowth phenomena. Within the DFT framework, Prestianni et al. 18 investigated subnanometric gold clusters, Au28, as catalysts involved in the oxygen-assisted selective dehydrogenation of the biomassderivedlignan hydroxymatairesinol (HMR) to oxomatairesinol (oxoMAT). Experimentally, it was found that the reactivity of the two diastereomers (RRR-HMR and SRR-HMR) isdi? erent, with SRR-HMR being more reactive than RRR-HMR. This evidence was explainedby means of a detailed description of all the molecular events (see Figure 1) taking place inthe reaction mechanism.

The computational approach straightforwardly highlighted that, if molecular oxygen is adsorbed on Au28 a double dehydrogenation occurs, via a concertedmechanism characterized by a six-membered ring transition state. However, analyzing theoptimized structures of the reactant molecule, the authors demonstrated that only the SRRHMRhas the appropriate geometry to transfer simultaneously two hydrogen to the activatedoxygen molecule adsorbed on the Au28 cluster. Depending on the type of support and the peculiar interactions with it, the subnanometriccluster could be charged; in this study, support e? ects were evaluated, modeling thecluster back-to the support electron charge transfer, taking into account a positively chargedgold cluster, (Au28)+3. With this approach, authors explained the experimentally observeddi? erences in reactivity, which take place when catalyst is formed by gold particles depositedon alumina with respect to those adsorbed on reducible supports as the cerium oxide one10. Indeed, generating positive charges on gold particles indeed inhibits electronic charge transfersto oxygen molecules adsorbed on gold hence precluding the activation of the O-O bondand, with this, decreasing the dehydrogenation rate.

Figure 1 about here. Several examples of the combination of theoretical calculations, on subnanometric metalcluster, with experimental studies deal with the unusual low temperature CO oxidationactivity37. Despite the large e? orts made to explain the catalytic activity of gold subnanoparticles, the origin of the low-temperature oxidation of CO on supported Au clustersis not yet completely unravelled. Di? erent possible factors were invoked, including size andoxidation state of the Au clusters as well as the chemical nature of the support. Several abinitio calculations were performed in order to model gold clusters of increasing size11, 38, 39and adsorption of O2 and CO on them31, 40, 41. As an example Prestianni et al. 41 evaluated all the elementary steps characterizing theoxygen-assisted CO oxidation on an Au13 cluster both uncharged and charged (cationic).

The reason behind the use of di? erently charged model for the catalyst resides, as mentionedabove, in the implicit evaluation of the influence of a possible charge transfer from the metalcluster to the support. On the grounds of the obtained DFT-based results, CO oxidationwas proposed to be likely to occur, even if with di? erent reaction paths, on both neutral andcharged cluster. On neutral Au13 clusters, the formation of an adduct containing a weaklybound O2, not a fully formed carbon dioxide molecule, was however observed. The adsorptionof a second CO molecule determined the facile desorption of CO2. On a cationic Au133+cluster, instead, the interaction between CO and O2, caused cleavage of the O2 molecule. The derived intermediate was characterized by a carbonate-like geometry, in agreement withpretty recent theoretical and experimental results42–44. According to the stoichiometry ofcarbon monoxide oxidation, two carbon dioxide molecules are produced from the reaction oftwo CO molecules with O2.

Modeling of the support might also involve the explicit evaluation of a particular exposedsurface where the subnanometric metal cluster is adsorbed. As an example, Schimmenti etal. 45 have studied, by means of periodic DFT-based calculations at the PBE+D3 level, thecatalytic activity toward formic acid decomposition of a subnanometric Pd6 cluster supportedon a hexagonal boron nitride (h-BN) monolayer. The DFT calculated energy profile for this process is reported in Figure 2, while theactivation barriers of selected dehydrogenation steps are reported in Figure 3, 4, 5, 6 alongwith the most relevant geometric descriptors of the involved species. Formic acid (HCOOH) is an important biomass-derived molecule that in the last few yearswas extensively studied by both the experimental and computational catalysis community, due to its potential use as viable source of hydrogen. Indeed, it is well known that HCOOHdecomposes to H2 and CO2 in presence of supported metal catalysts, such as Pd, Pt, Ni, Cu. The decomposition mechanism was previously studied for a variety of catalytic systems: according to the literature, HCOOH can decompose following two main paths, namely theformate (HCOO) and the carboxyl (COOH) pathways. Avoiding the latter hence reducingthe production of COOH could be particularly valuable for developing new active catalystsfor HCOOH decomposition.

COOH is indeed the main source of CO production during thereaction, that could act as a poison for the catalytic sites46–48. Periodic DFT calculationswere already employed in the past to address this issue, especially in the case of extendedmetal surfaces. Taking Pd as an example, a lot of e? orts were made to rationalize theHCOOH decomposition reaction mechanism and its energetics, with a special interest onstructure sensitivity49–52. These works mainly focus on the stability of HCOO and COOHthat actually might be a? ected by the catalyst surface site coordination, being HCOO morestable on more open surfaces. Therefore, it is possible to say that for subnanometric clustersthis concept could be extended to the limiting case of catalytic sites having an almost atomiccharacter45. Nucleation and growth processesThe catalyst support should allow the optimal dispersion of the active component, goodaccessibility and stability against sintering.

Silica, titania, alumina, and porous carbon aretypical examples of supports. However, organic polymers can also be used efficiently as solidsupports13, 53. The nucleation and growth of small palladium clusters, up to Pd9, into amicrocavity of porous hyper-cross-linked polystyrene (HPS) was investigated (Figure 7), bymeans of an hybrid approach (QM/MM) including the integration of DFT-based calculationsand molecular mechanics simulations13. Figure 7 about here. The geometries and the electronic structures of the palladium subnanometric clustersinside the HPS cavity, obtained following the one-by-one atom addition, were found to bea? ected mainly by the counterbalance between the Pd-phenyl and the Pd-Pd interactions. The analysis performed on energetics, cavity distortions, and cluster geometries, indeed, suggeststhat the cluster growth is dominated by the Pd-phenyl interactions up to the formationof Pd4 aggregates, whereas the metal-metal interactions start to rule the growth when theclusters become larger.

The elasticity of the HPS matrix also plays an important role in thecluster growth process, because it allows the distortion of the cavity when the Pd clustersare nucleating. This demonstrated that the HPS does not prevent particle sintering. Itssmall cavities a? ect the geometrical and electronic properties of the cluster (with respect tothe isolated clusters) and likely the overall catalytic properties.

By a similar procedure, using a periodic DFT approach and depositing Au atoms oneby-one on a CeO2 surface, Zhang et al. 10 obtained a detailed nucleation pattern of small Auclusters (up to Au11). On the grounds of this nucleation pattern, the authors identified boththe polymorphic fcc and hcp packing. This implies that the fcc-like and hcp-like clustershave similar energies. Moreover, they find that the contact-layer Au atoms, forming bondswith oxygen atoms belonging to the surface, are characterized by a positive charge, evenwhen overlaid by other Au atoms, in the case of larger cluster. Achieving a well established procedure for the synthesis of shape and size-controlledclusters is a widely discussed topic in literature.

From this point of view the honeycombstructure of the B3N3 rings in the boron nitride nanotubes (BNNT), could in principle generateinteresting template e? ects toward subnanometric metal clusters. To deepen this topic, Schimmenti et al. 54 performed a computational study elucidating how the metal-BNNT interactionsmight a? ect growing and shaping of Pd subnanoparticle. With a QM/MM approachexploiting the 2-layer ONIOM (our own n-layered integrated molecular orbital and molecularmechanics) energy extrapolation scheme, joined with a growth algorithm, authors inferredthat the establishment of favorable Pd-N interactions is, on the whole, as important as theretention of Pd-Pd interactions.

In correspondence of the defective zones of the support, especially vacancies, it is wellknown that nucleation and growth of metal clusters is eased. The periodicity of the latticemight influence shape and size also in the case of bimetallic subnanometric cluster. In orderto investigate the growth of ultra small homo- and hetero-nuclear metal clusters (up to Me4; Ni, Pd, Re, Pt, and NiPd, RePt), periodic DFT calculations were performed to simulatetheir nucleation on a defective graphene sheet, having one vacant site 15. Authors discussedthe results in terms of competition between metal-metal and metal-carbon interactions andcohesive energies of the metallic cluster formed; the integration of these two aspects allowedto define an energy descriptor: the nucleation energy. As a general trend, it was observedthat to a higher bulk cohesive energy of the metal corresponds a less distorted structureof the supported cluster and a higher nucleation energy, which instead decreases with theincrease of the affinity of the involved metal atoms toward the defect-free graphene.

Furthermore, the analysis of the structural characteristics suggested that when the metalmetalinteractions prevail on the metal-carbon ones, the nucleated cluster adopts, after somedistortions, the same geometry shown in the isolated state, leading to a surface species notvery di? erent with respect to that obtained with the simple chemisorption of a preformedclusters. Conversely, if metal-metal and metal-carbon interactions have comparable inten-sity, growth process usually leads to cluster geometries that could correspond to metastablestructures in the isolated state. This behavior can clearly a? ect the shape, of larger metalclusters on graphene. Finally, the authors hypothesized that since the graphene defectivesites are powerful nucleating centers, a graphene sheet having many vacant sites should allowthe generation of a large number of small metal clusters, with potential applications in thefield of catalysis and hydrogen storage molecular devices.

Sequencing of molecular eventsThe subnanometric size of the catalytic system enables also the possibility of evaluate allthe competitive routes taking place in a given catalytic process. As an example, Cortese etal. 55 studied the ethylene glycol decomposition on a Pd12 cluster. The size of the investigatedsystem allowed authors to explore by means of computational techniques almost allthe reactive routes associated with this process.

This determined the generation of a largegrid of possible events, useful to deepen the energetic ordering of di? erent reaction pathwaysthat in principle would let to isolate the whole reaction mechanism, involving manyand complexly tangled molecular events. So, to e? ectively analyze the decomposition path, not just the elementary steps involved in the reaction network but also their hypotheticalsequences, in the largest ensemble of their possible combinations, were accurately characterized. Within a graph theory (GT) based approach, authors analyzed all the pathwaysstarting from CH2OHCH2OH and leading to CO and H2. This allowed to draw a picture ofall the competitive routes leading to hydrogen production on a subnanometric Pd cluster. The total energy content (TEC) defined as the summation of all the activation barriers involvedin the development of a given route, was used as a heuristic energetic descriptor toorder all the found pathways.

The lowest TEC values found were employed to state thatamong the 41 possible paths those represented in Figure 8 were the most favorable ones.