

# Hakkinen oxygen-assisted selective dehydrogenation of the biomass-derived lignan hy...

[Environment](#), [Air](#)



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34 individuated three main factors that could rule the reactivity of supported subnanometric clusters: electronic characteristics, cluster fluxionality (i. e. cluster reconstruction caused 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 effects as clearly explained by Campbell et al. 35 in a revisitation of the well known Strong Metal Support Interaction (SMSI) effects. It should be stressed that these effects could assume much more importance in the subnanometric regime since, for cluster of 6-10 atoms, the number of 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 the overall properties of the catalysts. In a pretty recent letter of Ahmadi et al. 36, they proposed the following list of important effects exerted by the support:

- charge transfer from the support (or viceversa);
- perimeter activation and synergistic interactions.

Due to their different environment, metallic atoms at the support interface could show different reactivity. Moreover, vicinal support atoms could contribute to the reaction progress, providing adsorption sites for the reactants;

- structural changes in the subnanoparticle. Geometry of isolated and supported metallic clusters may significantly vary. In a more general view, metal-support interactions may contribute to rule shapes and sizes of the supported clusters, controlling nucleation and growth phenomena. Within the DFT framework, Prestianni et al. 18 investigated subnanometric gold

clusters, Au<sub>28</sub>, as catalysts involved in the oxygen-assisted selective dehydrogenation of the biomass-derived lignan hydroxymatairesinol (HMR) to oxomatairesinol (oxoMAT). Experimentally, it was found that the reactivity of the two diastereomers (RRR-HMR and SRR-HMR) is different, with SRR-HMR being more reactive than RRR-HMR. This evidence was explained by means of a detailed description of all the molecular events (see Figure 1) taking place in the reaction mechanism.

The computational approach straightforwardly highlighted that, if molecular oxygen is adsorbed on Au<sub>28</sub> a double dehydrogenation occurs, via a concerted mechanism characterized by a six-membered ring transition state. However, analyzing the optimized structures of the reactant molecule, the authors demonstrated that only the SRRHMR has the appropriate geometry to transfer simultaneously two hydrogen to the activated oxygen molecule adsorbed on the Au<sub>28</sub> cluster. Depending on the type of support and the peculiar interactions with it, the subnanometric cluster could be charged; in this study, support effects were evaluated, modeling the cluster back to the support electron charge transfer, taking into account a positively charged gold cluster, (Au<sub>28</sub>)<sup>+3</sup>. With this approach, authors explained the experimentally observed differences in reactivity, which take place when catalyst is formed by gold particles deposited on alumina with respect to those adsorbed on reducible supports as the cerium oxide one<sup>10</sup>. Indeed, generating positive charges on gold particles indeed inhibits electronic charge transfer to oxygen molecules adsorbed on gold hence precluding the

activation of the O-O bond and, with this, decreasing the dehydrogenation rate.

Figure 1 about here. Several examples of the combination of theoretical calculations, on subnanometric metal cluster, with experimental studies deal with the unusual low temperature CO oxidation activity<sup>37</sup>. Despite the large efforts made to explain the catalytic activity of gold subnanoparticles, the origin of the low-temperature oxidation of CO on supported Au clusters is not yet completely unravelled. Different possible factors were invoked, including size and oxidation state of the Au clusters as well as the chemical nature of the support. Several ab initio calculations were performed in order to model gold clusters of increasing size<sup>11, 38, 39</sup> and adsorption of O<sub>2</sub> and CO on them<sup>31, 40, 41</sup>. As an example Prestianni et al. <sup>41</sup> evaluated all the elementary steps characterizing the oxygen-assisted CO oxidation on an Au<sub>13</sub> cluster both uncharged and charged (cationic).

The reason behind the use of differently charged model for the catalyst resides, as mentioned above, in the implicit evaluation of the influence of a possible charge transfer from the metal cluster to the support. On the grounds of the obtained DFT-based results, CO oxidation was proposed to be likely to occur, even if with different reaction paths, on both neutral and charged cluster. On neutral Au<sub>13</sub> clusters, the formation of an adduct containing a weakly bound O<sub>2</sub>, not a fully formed carbon dioxide molecule, was however observed. The adsorption of a second CO molecule determined the facile desorption of CO<sub>2</sub>. On a cationic Au<sub>13</sub><sup>3+</sup> cluster, instead, the interaction between CO and O<sub>2</sub>, caused cleavage of the O<sub>2</sub> molecule. The

derived intermediate was characterized by a carbonate-like geometry, in agreement with pretty recent theoretical and experimental results<sup>42-44</sup>. According to the stoichiometry of carbon monoxide oxidation, two carbon dioxide molecules are produced from the reaction of two CO molecules with O<sub>2</sub>.

Modeling of the support might also involve the explicit evaluation of a particular exposed surface where the subnanometric metal cluster is adsorbed. As an example, Schimmenti et al.<sup>45</sup> have studied, by means of periodic DFT-based calculations at the PBE+D3 level, the catalytic activity toward formic acid decomposition of a subnanometric Pd<sub>6</sub> cluster supported on a hexagonal boron nitride (h-BN) monolayer. The DFT calculated energy profile for this process is reported in Figure 2, while the activation barriers of selected dehydrogenation steps are reported in Figure 3, 4, 5, 6 along with the most relevant geometric descriptors of the involved species. Formic acid (HCOOH) is an important biomass-derived molecule that in the last few years was 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 HCOOH decomposes to H<sub>2</sub> and CO<sub>2</sub> 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 the formate (HCOO) and the carboxyl (COOH) pathways. Avoiding the latter hence reducing the production

of COOH could be particularly valuable for developing new active catalysts for HCOOH decomposition.

COOH is indeed the main source of CO production during the reaction, that could act as a poison for the catalytic sites<sup>46–48</sup>. Periodic DFT calculations were already employed in the past to address this issue, especially in the case of extended metal surfaces. Taking Pd as an example, a lot of efforts were made to rationalize the HCOOH decomposition reaction mechanism and its energetics, with a special interest on structure sensitivity<sup>49–52</sup>. These works mainly focus on the stability of HCOO and COOH that actually might be affected by the catalyst surface site coordination, being HCOO more stable on more open surfaces. Therefore, it is possible to say that for subnanometric clusters this concept could be extended to the limiting case of catalytic sites having an almost atomic character<sup>45</sup>. Nucleation and growth processes The catalyst support should allow the optimal dispersion of the active component, good accessibility and stability against sintering.

Silica, titania, alumina, and porous carbon are typical examples of supports. However, organic polymers can also be used efficiently as solid supports<sup>13, 53</sup>. The nucleation and growth of small palladium clusters, up to Pd<sub>9</sub>, into a microcavity of porous hyper-cross-linked polystyrene (HPS) was investigated (Figure 7), by means of a hybrid approach (QM/MM) including the integration of DFT-based calculations and molecular mechanics simulations<sup>13</sup>. Figure 7 about here. The geometries and the electronic structures of the palladium subnanometric clusters inside the HPS cavity,

obtained following the one-by-one atom addition, were found to be affected mainly by the counterbalance between the Pd-phenyl and the Pd-Pd interactions. The analysis performed on energetics, cavity distortions, and cluster geometries, indeed, suggests that the cluster growth is dominated by the Pd-phenyl interactions up to the formation of Pd<sub>4</sub> aggregates, whereas the metal-metal interactions start to rule the growth when the clusters become larger.

The elasticity of the HPS matrix also plays an important role in the cluster growth process, because it allows the distortion of the cavity when the Pd clusters are nucleating. This demonstrated that the HPS does not prevent particle sintering. Its small cavities affect the geometrical and electronic properties of the cluster (with respect to the isolated clusters) and likely the overall catalytic properties.

By a similar procedure, using a periodic DFT approach and depositing Au atoms one-by-one on a CeO<sub>2</sub> surface, Zhang et al. 10 obtained a detailed nucleation pattern of small Au clusters (up to Au<sub>11</sub>). On the grounds of this nucleation pattern, the authors identified both the polymorphic fcc and hcp packing. This implies that the fcc-like and hcp-like clusters have similar energies. Moreover, they find that the contact-layer Au atoms, forming bonds with oxygen atoms belonging to the surface, are characterized by a positive charge, even when overlaid by other Au atoms, in the case of larger cluster. Achieving a well established procedure for the synthesis of shape and size-controlled clusters is a widely discussed topic in literature.

From this point of view the honeycomb structure of the B<sub>3</sub>N<sub>3</sub> rings in the boron nitride nanotubes (BNNT), could in principle generate interesting template effects toward subnanometric metal clusters. To deepen this topic, Schimmenti et al. 54 performed a computational study elucidating how the metal-BNNT interactions might affect growing and shaping of Pd subnanoparticle. With a QM/MM approach exploiting the 2-layer ONIOM (our own n-layered integrated molecular orbital and molecular mechanics) energy extrapolation scheme, joined with a growth algorithm, authors inferred that the establishment of favorable Pd-N interactions is, on the whole, as important as the retention of Pd-Pd interactions.

In correspondence of the defective zones of the support, especially vacancies, it is well known that nucleation and growth of metal clusters is eased. The periodicity of the lattice might influence shape and size also in the case of bimetallic subnanometric cluster. In order to investigate the growth of ultra small homo- and hetero-nuclear metal clusters (up to Me<sub>4</sub>; Ni, Pd, Re, Pt, and NiPd, RePt), periodic DFT calculations were performed to simulate their nucleation on a defective graphene sheet, having one vacant site 15. Authors discussed the results in terms of competition between metal-metal and metal-carbon interactions and cohesive energies of the metallic cluster formed; the integration of these two aspects allowed to define an energy descriptor: the nucleation energy. As a general trend, it was observed that to a higher bulk cohesive energy of the metal corresponds a less distorted structure of the supported cluster and a higher nucleation



energy, which instead decreases with the increase of the affinity of the involved metal atoms toward the defect-free graphene.

Furthermore, the analysis of the structural characteristics suggested that when the metal-metal interactions prevail on the metal-carbon ones, the nucleated cluster adopts, after some distortions, the same geometry shown in the isolated state, leading to a surface species not very different with respect to that obtained with the simple chemisorption of a preformed cluster. Conversely, if metal-metal and metal-carbon interactions have comparable intensity, growth process usually leads to cluster geometries that could correspond to metastable structures in the isolated state. This behavior can clearly affect the shape, of larger metal clusters on graphene. Finally, the authors hypothesized that since the graphene defective sites are powerful nucleating centers, a graphene sheet having many vacant sites should allow the generation of a large number of small metal clusters, with potential applications in the field of catalysis and hydrogen storage molecular devices.

**Sequencing of molecular events** The subnanometric size of the catalytic system enables also the possibility of evaluate all the competitive routes taking place in a given catalytic process. As an example, Cortese et al. 55 studied the ethylene glycol decomposition on a Pd<sub>12</sub> cluster. The size of the investigated system allowed authors to explore by means of computational techniques almost all the reactive routes associated with this process.

This determined the generation of a large grid of possible events, useful to deepen the energetic ordering of different reaction pathways that in principle would let to isolate the whole reaction mechanism, involving many and complexly tangled molecular events. So, to effectively analyze the decomposition path, not just the elementary steps involved in the reaction network but also their hypothetical sequences, in the largest ensemble of their possible combinations, were accurately characterized. Within a graph theory (GT) based approach, authors analyzed all the pathways starting from  $\text{CH}_2\text{OHCH}_2\text{OH}$  and leading to  $\text{CO}$  and  $\text{H}_2$ . This allowed to draw a picture of all 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 involved in the development of a given route, was used as a heuristic energetic descriptor to order all the found pathways.

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