Cite this: DOI: 10.1039/d2fd90085h

DISCUSSIONS



View Article Online View Journal

Nanoalloy structures and catalysis part 1: general discussion

Damien Alloyeau, Vincenzo Amendola, Catherine Amiens, Pascal Andreazza, Joost M. Bakker, Francesca Baletto, Stephan Barcikowski, Noelia Barrabés, Michael Bowker, D Fuyi Chen, Emmanuel Cottancin, Wolfgang E. Ernst, Riccardo Ferrando, Georg Daniel Förster, Alessandro Fortunelli, D Didier Grandjean, Hazar Guesmi, Graham J. Hutchings, Ewald Janssens, Miguel Jose Yacaman, Christian Kuttner, Lebohang Macheli, Éric Marceau, Marcelo M. Mariscal, Jette K. Mathiesen, John McGrady, Christine Mottet, Diana Nelli, Pinkie Ntola, Cameron J. Owen, Micha Polak, Jonathan Quinson, Cesare Roncaglia, Leonid Rubinovich, Rolf Schäfer, Manoj Settem, Jeff Shield, Mzamo Shozi, Swathi Swaminathan, Štefan Vajda Angelan, Manas-Christian Weissker

DOI: 10.1039/d2fd90085h

Nanoalloy structures, part 1

Graham J. Hutchings opened discussion of the introductory lecture by Miguel Jose Yacaman: In your presentation (https://doi.org/10.1039/d2fd00137c), you showed good examples of strain in unsupported nanoparticles. What happens to the strain when the nanoparticles are supported?

Miguel Jose Yacaman replied: Of course that is a very different situation. If the support is weakly interacting with the nanoparticle, no effect is expected. However, if the substrate-particle interaction is strong, we expect the strain to be changed. We have not obtained data on this case.

Ewald Janssens commented: A careful study of multimetallic nanoalloys is challenging, both computationally and experimentally. From your presentation (https://doi.org/10.1039/d2fd00137c), it is obvious that there are many interesting fundamental questions concerning the structure and properties of multimetallic nanoalloys. Concrete future uses would strengthen the arguments to convince funding agencies to invest more in this research. In which application fields is it highly likely that multimetallic nanoalloys will be able to outperform monometallic or bimetallic nanoparticles?

Stephan Barcikowski responded: A relevant perspective article, mainly on the binary systems made by laser synthesis for use in heterogeneous catalysis, has been published as ref. 1. Personally, I think that having more elements provides the required span of active-site types, and this is currently an active area in highentropy alloy (HEA) nanoparticle electrocatalysis. Here, one should keep an eye on noble-metal-free HEAs, and also on the durability of the catalyst. There are several recent reviews on HEA catalysis with 5 or more elements. Theory will have an important role in the future of that field.

Leonid Rubinovich asked: Are the distinct strain features related to the alloy's atomic mismatch?

Miguel Jose Yacaman replied: Yes, but strain is also modulated by the entropy.

Christian Kuttner commented: You presented the fascinating example of Pt–Ni nanoalloy particles with a stripe-like variation in composition. Did I understand correctly that strain is the main driving force for this composition modulation? Can this modulation be controlled and how does it affect the properties?

Miguel Jose Yacaman responded: The variation is due to the interplay of entropy and strain.

Jette K. Mathiesen asked: When introducing more elements, do you believe that we can solely rely on entropy as a driving force to obtain a high degree of elemental mixing? Or is it necessary to introduce high temperatures or other effects to promote mixing?

Miguel Jose Yacaman responded: The entropy is important, but is not the only factor. The internal strain and the creation of twin boundaries also contribute to the Gibbs free energy. However, if the temperature is increased, the entropy increases and the strain decreases because partial dislocations will move to the surface. However, the twin-boundary energy still remains large.

Manoj Settem remarked: I have a question related to disclinations. Disclinations are very stable at the nanoscale; for example, the penta-twin in a decahedron-shaped structure, which consists of five Σ 3 grain boundaries. Is there a possibility of disclinations different to a penta-twin, and having other coincidence site lattice (CSL) boundaries, being either stable or metastable in nanoparticles of sizes < 10 nm?

Miguel Jose Yacaman replied: It is now well established that, in a decahedral nanoparticle, the stress will be produced in the so-called 2 + 2 + 1 configuration. That means that 2 sets of tetrahedra will have the same stress configuration and one will be different. So it is not as simple as the old single-disclination model.

S. Reichenberger, G. Marzun, M. Muhler and S. Barcikowski, Perspective of Surfactant-Free Colloidal Nanoparticles in Heterogeneous Catalysis, *ChemCatChem*, 2019, **11**, 4489–4518, DOI: **10.1002/cctc.201900666**.





Strain has been mapped using precession diffraction. Two examples are shown in Fig. 1.

Graham J. Hutchings remarked: You mentioned that no one was able to make silver nanoparticles that could be used for cancer treatment. In catalysis, we accept that the nanoparticles we prepare will have a particle size distribution and we use this effectively. Is the precision in the silver particles really needed?

Miguel Jose Yacaman answered: We have used silver nanoparticles as SERS substrates for a biomarker cancer test. The health regulatory bodies require that the nanoparticles are certified. In other words, that they always produce a reliable SERS signal. The size is not important but rather the ability of the analyte molecules to attach to the silver nanoparticle surface. You have to prove to the regulatory body that no false negatives are introduced by the nanoparticles.

Christian Kuttner said: You have shown the transition to plasmonic behavior in nanoalloy particles. Is this primarily a size effect or does the local composition at the surface also matter?

Miguel Jose Yacaman answered: This is a size effect and it is related to the fact that when the number of atoms increases, the electron scattering becomes coherent and Bloch waves are formed. The result is the formation of bands that, in the case of metals, overlap. This is only a function of the number of atoms.

Christine Mottet commented: My question is about the correlation between twins and dislocations. From my point of view, twins are static, whereas dislocations are moving. What is the correlation between dislocations and twins in nanoparticles that you refer to in your presentation (https://doi.org/10.1039/d2fd00137c)?

Miguel Jose Yacaman answered: I mean that when strain is formed inside a multimetallic nanoparticle, partial dislocations will be formed that tend to move to the surface. A twin is created by this movement. Hazar Guesmi asked: Is there any evidence of the stability of the phase structures and/or strained domains in HEAs under *in situ/operando* conditions?

Miguel Jose Yacaman answered: Not yet. However, it will be necessary to use an ultrasensitive CMOS camera to obtain high-angle annular dark field (HAADF)-STEM images *in situ*. This is, however, totally possible.

Didier Grandjean asked: Regarding the *in situ* behaviour of nanoalloy-based catalysts, is it (or will it be) possible to predict theoretically some of the structural transformation(s) that a nanoalloy of a given structure under ambient conditions will undergo when it is placed under particular gas and temperature conditions?

Miguel Jose Yacaman replied: I believe that this will be possible. As we know, during reactions the surfaces are "cleaned" and they look like surfaces in UHV. The challenges for theoretical calculations will be to find a good interatomic potential for multimetallic systems and calculate the entropy contribution.

Wolfgang E. Ernst opened a discussion of the paper by Marcelo M. Mariscal: In your indentation experiments (https://doi.org/10.1039/d2fd00111j), the electron beam of the electron microscope is directed vertically to the direction of pressure, *i.e.*, passing through the gap. How large is this gap (*i.e.*, the size of the nanoparticle pressed) and what is the resolution of the electron microscope image? Does it allow for determination of the changes in bond distances due to the pressure?

Marcelo M. Mariscal replied: TEM images were recorded with a JEOL 2010 microscope working at 200 kV in TEM and dark-field modes. For the dark-field images, the smaller objective aperture was placed slightly off with reference to the transmitted beam to collect diffraction spots of a group of reflections up to the second order.

At the present resolution, bond-distance changes are unable to be detected.

Damien Alloyeau remarked: Your simulations are performed on 10 nm nanoparticles. Do you expect to see size effects in your results if you use larger nanoparticles (20 to 50 nm)?

Is it possible to perform nanoindentation TEM measurements on sub-10 nm nanoparticles?

Marcelo M. Mariscal responded: A size effect is not expected if the simulated nanoparticle increases in size, but it will be better to simulate nanoparticles with sizes close to experimental ones.

Cameron J. Owen asked: Do you have a quantitative understanding of the force prediction error?

Marcelo M. Mariscal answered: No, but it could be estimated by means of calculation of the variance of the force measurements.

Jonathan Quinson commented: In your conclusion, you state that having the harder material on the outer part of the alloy would achieve the highest

View Article Online Faraday Discussions

Discussions

mechanical resistance (in the case of core–shell nanoparticles). Maybe I missed it but I am wondering if you know/can estimate after how many layers of atoms this effect starts to be observable, and how this critical number of atomic layers is expected to change with the size of the nanoparticles?

Marcelo M. Mariscal responded: As can be observed in Fig. 2a of our paper (https://doi.org/10.1039/d2fd00111j), the yield strengths of the different particle compositions of Ni_xCo (x = 12.5; 25) are near each other, and the number of atomic layers parallel to the indenter to reach the core are 11 and 6, respectively. The Ni_{12.5}Co nanoparticles have 14 layers. Due to the similar lattice and cohesive energy properties of the elements that compose the nanoparticle, the number of expected layers cannot be determined easily.

Francesca Baletto asked: Have you calculated the velocity of the dislocation? Is there any effect on the initial shape of the nanoalloys? Can you discuss the effect of the chemical ordering?

Marcelo M. Mariscal answered: We haven't calculated the dislocation speed, however, it is very easy to estimate. Thanks for your query.

Jeff Shield asked: Did you observe any dislocations in the as-made nanoparticles? If not, were you able to quantify the yield stress, as it should approach the theoretical limit of $G/2\pi$, where *G* is the shear modulus? Were the dislocations in the core–shell structure misfit dislocations?

Marcelo M. Mariscal responded: No dislocation was observed when the nanoparticle was relaxed. Due to a similar lattice constant, little misfits can be found in the interface, but they are not enough to generate a distortion at the interface.

Rolf Schäfer asked: Why was a square law of distance used for the external repulsive force exerted by the indenter? Wouldn't it make more sense to start with a linear dependence (harmonic approximation) and add anharmonic contributions in the next step?

Marcelo M. Mariscal responded: The applied external force is determined by the LAMMPS program.¹ The way in which the indenter applies a force in the particles depends on how deep the atom is in the indenter region. During all the indentation, the maximum quantity of atoms in the indenter region is the number of island atoms of the nanoparticle near the indenter.

1 https://docs.lammps.org/fix_indent.html.

Alessandro Fortunelli remarked: Your energy/strain curves show plastic collapses (drops in energy) that are quantitatively quite different from one system to another.

Is the size of the energy drop correlated with the metastability of the investigated configuration, *i.e.*, whether they are closer or farther from the thermodynamic global minimum?

Also, can you connect these collapses with energy barriers to create the given plastic deformation (dislocation), see, *e.g.*, ref. 1 and 2?

- 1 A. Fortunelli, Simulation of the plastic behavior of amorphous glassy bis-phenol-*A*-polycarbonate, *J. Chem. Phys.*, 2004, **121**, 4941, DOI: **10.1063/1.1778157**.
- 2 A. Fortunelli and M. Ortiz, Constitutive model for plasticity in an amorphous polycarbonate, *Phys. Rev. E*, 2007, **76**, 041806, DOI: **10.1103/PhysRevE.76.041806**.

Marcelo M. Mariscal replied: Thanks, it is an interesting question. However, we don't have any evidence at the moment to completely answer this question. We believe that there exists a direct correlation between the energy drops during plastic deformation and the energy barriers for dislocation formation, but this merits further detailed research.

Micha Polak asked: For NiCo, why are the slopes of the elastic and plastic regions of the force–strain curves very similar?

Marcelo M. Mariscal answered: In the bulk theoretical studies, the lattice parameter and the cohesive energy of the monometallic metals are very similar. The force-strain curves are similar due to that.

Riccardo Ferrando remarked: Your molecular dynamics (MD) simulations were made at room temperature. Have you tried to look at the evolution of the system at higher temperatures? Since the timescale of MD has clear limitations, simulations at higher temperatures can be useful for collecting information about possible processes whose typical timescales are too long to be detected by MD at room temperature.

Marcelo M. Mariscal responded: The indentation of the nanoparticles was only done at room temperature. Thanks for your recommendation, we will try MD simulations at higher temperatures.

Cesare Roncaglia asked: In the paper (https://doi.org/10.1039/d2fd00111j), some mechanisms for the dynamics of dislocations in a spherical nanoalloy are presented and discussed. Do you have any particular expectation for other geometrical structures, such as icosahedral and decahedral nanoalloys?

Marcelo M. Mariscal replied: It is an interesting question that merits further research to be answered. However, in a previous work where we studied cubic nanoparticles, the nucleation of Shockley partial dislocations (SPDs) starts at the corner instead of the pole of the sphere like here. So, it is expected that the nucleation of dislocations changes with the geometry of the nanoalloys.

Pinkie Ntola communicated: Very insightful talk. What informed the different compositions of the alloy mixtures? It would be interesting to see how the mechanical response changes with more varied compositions. *E.g.*, swapping the ratios around for Ni and Co.

Marcelo M. Mariscal communicated in reply: Thanks, it is an interesting question that merits further research to be answered.

View Article Online Faraday Discussions

Discussions

Fuyi Chen communicated: After NiCo is formed into an isoentropy alloy by adding additional elements, such as Cr element, under the action of an external force, how do the generation of the dislocations, stacking faults and twins change in the nanoparticles?

Marcelo M. Mariscal communicated in reply: It is an interesting question that merits further research to be answered.

Mzamo Shozi communicated: Was there any correlation made between the Shockley partial dislocation densities and strain? If yes, what were the differences between the alloy mixtures and monometallic particles?

Marcelo M. Mariscal communicated in reply: Yes, we plotted the dislocation density together with SPD *vs.* strain. As observed in Fig. 2 and 3, a direct correlation can be found.

Vincenzo Amendola opened a discussion of the paper by Georg Daniel Förster: Thank you for your interesting talk.

We have synthesized Ag–Co nanoparticles with a larger size¹ than that considered in your study (https://doi.org/10.1039/d2fd00114d), and done the same for a Ag–Fe nanoalloy.^{2,3} While we had experimental evidence on multiple occasions of the homogeneous distribution of the two components in the alloys, the X-ray diffraction and high-resolution transmission electron microscopy analysis always indicated that the crystalline lattice remained that of pure Ag (face-centred cubic), without any distortion of the lattice parameter.^{1,2} We concluded that Co (or Fe) may be segregated in some ultrasmall domains, perhaps disordered, or on defect sites.^{1,2,4} Do you have any evidence that this may be the case, according to your calculations?

- 1 A. Guadagnini, S. Agnoli, D. Badocco, P. Pastore, D. Coral, M. B. Fernàndez van Raap, D. Forrer and V. Amendola, Facile synthesis by laser ablation in liquid of nonequilibrium cobalt-silver nanoparticles with magnetic and plasmonic properties, *J. Colloid Interface Sci.*, 2021, **585**, 267–275, DOI: **10.1016/j.jcis.2020.11.089**.
- 2 V. Amendola, S. Scaramuzza, S. Agnoli, G. Granozzi, M. Meneghetti, G. Campo, V. Bonanni, F. Pineider, C. Sangregorio, P. Ghigna, S. Polizzi, P. Riello, S. Fiameni and L. Nodari, Laser generation of iron-doped silver nanotruffles with magnetic and plasmonic properties, *Nano Res.*, 2015, 8, 4007–4023, DOI: 10.1007/s12274-015-0903-y.
- 3 S. Scaramuzza, S. Polizzi and V. Amendola, Magnetic tuning of SERS hot spots in polymercoated magnetic-plasmonic iron-silver nanoparticles, *Nanoscale Adv.*, 2019, **1**, 2681–2689, DOI: **10.1039/c9na00143c**.
- 4 V. Coviello, D. Forrer and V. Amendola, Recent Developments in Plasmonic Alloy Nanoparticles: Synthesis, Modelling, Properties and Applications, *ChemPhysChem*, 2022, 23, e202200136, DOI: 10.1002/cphc.202200136.

Georg Daniel Förster replied: I think this may very well be the case. In simulations where growth is simulated on preformed Co and Ag particles, small, relatively stable Co clusters form in the subsurface. Eventually, these Co clusters tend to aggregate in the center of the particles, but this may be delayed in the case of larger particles. However, I am not sure to what extent these results are transferable to synthesis in liquids since our simulations are under vacuum and at most take into account the interaction with an amorphous carbon substrate.



Fig. 2 Force vs. longitudinal strain curves for Co_xNi and Ni_xCo (core-shell).

Catherine Amiens asked: When cobalt clusters are deposited first on the amorphous carbon support, do you observe some carbon diffusion inside the cluster?

Random



Fig. 3 Force vs. longitudinal strain curves for Co_xNi and Ni_xCo (random).

Georg Daniel Förster replied: In our simulations, we did not observe carbon diffusion inside the Co clusters. Some of the cobalt atoms, however, diffused into the amorphous carbon substrate. From the experimental point of view, we also have no evidence of carbon inside the clusters. However, we would only have noticed this if there was a considerable amount of dissolved carbon in the particles. In any case, I don't want to make any strong claims about this, since we have not tried to study this specific fact.

Riccardo Ferrando said: Experimentally, AgCo nanoparticles are clearly threedimensional on the substrate, so the interaction with it should be considerably weaker than the metal-metal interactions.

Georg Daniel Förster responded: Although I consider our potential for interaction with the substrate to be a work in progress, we nevertheless obtain threedimensional particles comparable to what is observed experimentally. This is not surprising though, since we used the comparison with the experimental aspect ratios of pure Ag and Co particles as a reference for the parameterization of the potential.

Wolfgang E. Ernst remarked: When simulating effects of internal nanoparticle interactions, and interactions with a substrate, the size of the cluster or nanoparticle may make an important difference. The binding energy per atom of metal clusters grows with cluster size due to many-body interactions. So the binding energy per atom bound on the substrate may be larger than the internal cluster binding energy for small metal clusters, while, for large metal clusters, the internal binding may be stronger than the interaction with the substrate surface. For example, Au dimers, trimers, and tetramers have binding energies of approx. 1 to 1.5 eV per atom, while bulk Au has a binding energy of approx. 3.5 eV per atom. This makes a difference, when the binding to the substrate gives rise to a binding energy of approx. 1 eV per atom. Is this considered?

Georg Daniel Förster replied: Thank you very much for this comment. In this work (https://doi.org/10.1039/d2fd00114d), we did not consider multi-body effects for the interaction with the substrate, but I think, as you say, that it would be important to take them into account so that we can better describe particle growth under non-equilibrium conditions. We will be thinking about how to include these effects in future simulations of particle growth on substrates.

Micha Polak asked: Can the second moment approximation to the tight binding model (TB-SMA) be adapted for carbon-metal interactions? Are any difficulties anticipated regarding the parametrization?

Georg Daniel Förster replied: Clearly it can be adapted, and I think that's the best way to move forward. The reason why we have not done it until now was the lack of sufficient reference data. For interactions with the substrate, experimental reference data should be preferred in my opinion, as DFT results are too dependent on functionals in these situations due to long-range van der Waals interactions.

Jonathan Quinson remarked: I am not a theoretician (at all). I am wondering how much you could tune the parameters related to the support and how easy it would be to make it a "variable" in your study (https://doi.org/10.1039/d2fd00114d). I am wondering, for instance, if you could easily model nitrogendoped carbon (since nitrogen-doped carbon is known to induce different nucleation properties of a range of nanoparticles). And, therefore, to what extent your results could help in designing a support to get a given nanoparticle size, shape or composition (I am thinking, in particular, of the case of one-pot syntheses)?

Georg Daniel Förster responded: I must admit that I am not familiar with nitrogen-doped carbon. If it does indeed, as you say, significantly affect the nucleation properties, it would probably be necessary to develop a dedicated interatomic

model in order to be able to perform simulations similar to those we have presented, but with a nitrogen-doped carbon substrate. This would represent a considerable amount of work. However, it might also be possible to simply tune the interaction strength with the substrate, but I do not know enough about the system to be sure.

Francesca Baletto asked: Have you performed a layer-by-layer analysis of the supported nanoalloys? Please clarify how the *H*/*D* ratio mentioned in the article (https://doi.org/10.1039/d2fd00114d) is calculated.

Georg Daniel Förster replied: We did not analyze the particles layer-by-layer in a systematic way. Nevertheless, it appears from the simulations that the layer in contact with the substrate is silver, directly followed by the cobalt core. The H/D ratio (height/diameter ratio) was used to calibrate the interaction force with the substrate in the simulations by comparison with the X-ray diffraction data.

Cesare Roncaglia asked: Can you compare the values of α that you obtained in your simulations with some experimental results? It may be helpful for the determination (or improvement) of metal-carbon interaction parameters.

Georg Daniel Förster replied: At the moment, we have no experimental data on particle orientation. Yet, we have HRTEM images of the particles that we plan to analyze in terms of partial orientation using a deep learning approach in the very near future. This should allow for further comparisons with the simulations we have described.

Fuyi Chen communicated: Regarding the particle growth of Ag on Co, and Ag on Co, for carbon-supported particles, how do the Co–C binding and Ag–C binding affect the growth behavior?

Georg Daniel Förster communicated in reply: Simulations indicate that interactions with amorphous carbon (Ag–C and Co–C) lead to slightly flattened particles and that the core–shell structure of free AgCo nanoalloys is also affected. We find a single layer of Ag in direct contact with the substrate (as opposed to several layers in the case of free AgCo particles). The Co core is directly above this monolayer. Any excess Ag seems to accumulate on the side of the particles. However, this will have to be confirmed by experiments. Our current experimental data are not clear enough to make a statement on this point.

Swathi Swaminathan opened a discussion of the paper by Diana Nelli: The line-mapping image of the nanoparticle looks more like an alloy-type particle than a core–shell one.

Diana Nelli responded: Below you can find a list of experimental articles in which off-centered Pt-rich cores were shown.

- 1 C. K. Narula, et al., J. Phys. Chem. C, 2015, 119(44), 25114-25121.
- 2 S. I. Sanchez, et al., J. Am. Chem. Soc., 2009, 131(24), 8683-8689.
- 3 C. A. Rodriguez-Proenza, et al., Materials, 2018, 11(10), 1882.
- 4 A. K. Medina-Mendoza, et al., Mater. Chem. Phys., 2019, 228, 303-309.

⁵ D. Nelli, et al., Nanoscale Adv., 2021, 3, 836.

Alessandro Fortunelli remarked: Nice work.

In your simulations, did you observe any vacancy formation as a diffusion mechanism, see, *e.g.*, ref. 1?

Also, did you observe whether there is a size evolution of collective mechanisms that are common in small clusters see, *e.g.*, ref. 2?

1 F. Taherkhani, F. R. Negreiros, G. Parsafar and A. Fortunelli, Simulation of vacancy diffusion in a silver nanocluster, *Chem. Phys. Lett.*, 2010, **498**, 312–316, DOI: **10.1016**/ **j.cplett.2010.08.076**.

2 M. Asgari, F. R. Negreiros, L. Sementa, G. Barcaro, H. Behnejad and A. Fortunelli, Striking dependence of diffusion kinetics in Ag–Cu nanoalloys upon composition and quantum effects, *J. Chem. Phys.*, 2014, **141**, 041108, DOI: **10.1063/1.4891564**.

Diana Nelli answered: The formation of vacancies in nanoparticles and nanoalloys has been observed in several computational works. Vacancies can easily form close to the nanoparticle surface,^{1,2} but they can also appear directly in the inner region, as it was shown in the case of icosahedral nanoparticles.^{3,4} In the case of nanoalloys, vacancies can be involved in interdiffusion processes.^{1–5} In this case, we have not analysed in detail the elementary diffusion mechanisms responsible for the equilibration of chemical ordering. However, we expect vacancy-mediated diffusion mechanisms to take place in our simulations, especially in the case of icosahedral AuCu nanoalloys, in which the formation of internal vacancies can be induced by mechanisms like those described in ref. 3 and 4.

The evolution of shape and chemical arrangement of nanoparticles and nanoalloys is dominated by processes of collective character, in which multiple atoms are involved at the same time. Our molecular dynamics simulations have singled out the occurrence of collective mechanisms in nanoparticles that are much larger than those in ref. 6; for example, we can mention the reshaping processes occurring during the coalescence of two nanoparticles,^{7,8} and the shift of large islands on the surface of crystalline fcc nanoparticles.⁹ These processes involve several tens of atoms.

- 1 F. Delogu, The mechanism of chemical disordering in Cu₃Au nanometre-sized systems, *Nanotechnology*, 2007, **18**, 235706, DOI: **10.1088/0957-4484/18/23/235706**.
- 2 R. Ferrando, Mass Transport in Nanoalloys Studied by Atomistic Models, *Diffus. Found.*, 2017, 12, 23–37, DOI: 10.4028/www.scientific.net/DF.12.23.
- 3 D. Nelli, F. Pietrucci and R. Ferrando, Impurity diffusion in magic-size icosahedral clusters, *J. Chem. Phys.*, 2021, **155**, 144304, DOI: **10.1063/5.0060236**.
- 4 D. Nelli, Central vacancy creation in icosahedral nanoparticles induced by the displacement of large impurities, *Eur. Phys. J.: Appl. Phys.*, 2022, **97**, 18, DOI: **10.1051/epjap**/ 2022210282.
- 5 F. Taherkhani, F. R. Negreiros, G. Parsafar and A. Fortunelli, Simulation of vacancy diffusion in a silver nanocluster, *Chem. Phys. Lett.*, 2010, **498**, 312–316, DOI: **10.1016**/**j.cplett.2010.08.076**.
- 6 M. Asgari, F. R. Negreiros, L. Sementa, G. Barcaro, H. Behnejad and A. Fortunelli, Striking dependence of diffusion kinetics in Ag–Cu nanoalloys upon composition and quantum effects, *J. Chem. Phys.*, 2014, **141**, 041108, DOI: **10.1063/1.4891564**.
- 7 D. Nelli, G. Rossi, Z. Wang, R. E. Palmer and R. Ferrando, Structure and orientation effects in the coalescence of Au clusters, *Nanoscale*, 2020, **12**, 7688–7699, DOI: **10.1039**/ **c9nr10163b**.
- 8 D. Nelli, M. Cerbelaud, R. Ferrando and C. Minnai, Tuning the coalescence degree in the growth of Pt–Pd nanoalloys, *Nanoscale Adv.*, 2021, **3**, 836–846, DOI: **10.1039/d0na00891e**.
- 9 E. El koraychy, C. Roncaglia, D. Nelli, M. Cerbelaud and R. Ferrando, Growth mechanisms from tetrahedral seeds to multiply twinned Au nanoparticles revealed by atomistic simulations, *Nanoscale Horiz.*, 2022, **7**, 883–889, DOI: **10.1039/d1nh00599e**.

Christian Kuttner queried: Could you explain why diffusion in AgAu is faster than in PdPt? Is this just a direct consequence of the different cohesive energies? The local distribution should also play a role here, right?

Diana Nelli responded: The PtPd system is more cohesive than AgAu, therefore interdiffusion is significantly slower. Indeed, in order to observe similar interdiffusion rates, we had to simulate the evolution at different temperatures, which were much higher in the case of PtPd.

Though the local environment of each single atom is expected to somewhat affect its diffusion rate, our simulations show that diffusion processes are often of collective character, with the displacement of several atoms at the same time. In some cases, such collective processes produce significant changes in the overall chemical arrangement, without affecting the atomic local environment. A striking example is the sequence of diffusion processes that lead to the displacement of the core in Pt@Pd core@shell nanoalloys.

Micha Polak remarked: PtPd and AgAu have a non-negligible ordering/mixing tendency (~40–60 meV mixing enthalpies), which does not show up in reported phase diagrams. How is this tendency reflected in your modeling and the results? Why do Pt and Au go to the (respective) subsurfaces?

Diana Nelli responded: PtPd and AgAu are systems with a high tendency towards intermixing, both in the bulk and at the nanoscale. In nanoparticles, the surface is expected to be strongly enriched in Ag/Pd (which have lower surface energy compared to Au/Pt), as we have observed in our Monte Carlo simulations. This behaviour affects the overall chemical ordering pattern; specifically, the subsurface layer is enriched in Au/Pt in order to maximise the number of heterogeneous bonds.

Pascal Andreazza commented: In your paper (https://doi.org/10.1039/ d2fd00113f), you compare the temperature effect of AuCu clusters, initially in a core-shell configuration, for a truncated octahedral (TO) structure with respect to an icosahedral (Ih) structure. This core-shell configuration is clearly out of equilibrium. How do you explain the asymmetry of the disordering with a distorted zone formation (half of the cluster) in the case of the Ih, which is a more isotropic structure than TO?

Diana Nelli replied: The different behaviour of icosahedral (Ih) and truncated octahedral (TO) nanoparticles is indeed interesting, and deserves further investigation. We note that the tendency of the Ih to partially disorder on one side is quite general. In fact, the asymmetric deformation of the Ih structure has also been observed in our molecular dynamics simulations for pure Au nanoparticles.¹ In the case of Au, the Ih is highly unfavourable, therefore it quickly transforms into a lowest-energy decahedron (Dh) or TO. The first stage of the evolution is always the partial disordering of the structure; in the ordered part, the original icosahedral fivefold axes are maintained, whereas, on the opposite side, the surface is quite rough. Such a partially disordered Ih can evolve directly towards the Dh or TO, but sometimes it passes through a bi- or tri-Dh, with two or three decahedral fivefold axes. Out-of-equilibrium TO nanoparticles exhibit a different evolution pathway, in which disordering is achieved isotropically through the

formation of a structure that resembles a liquid droplet. Liquid-like structures, like those in Fig. 9(b) of the paper (https://doi.org/10.1039/d2fd00113f), have also been observed during the evolution of AuCo and AgNi nanoparticles.²

- 1 D. Nelli, G. Rossi, Z. Wang, R. E. Palmer and R. Ferrando, Structure and orientation effects in the coalescence of Au clusters, *Nanoscale*, 2020, **12**, 7688–7699, DOI: **10.1039**/**c9nr10163b**.
- 2 D. Nelli and R. Ferrando, Core-shell vs. multi-shell formation in nanoalloy evolution from disordered configurations, *Nanoscale*, 2019, **11**, 13040–13050, DOI: **10.1039/c9nr02963j**.

Emmanuel Cottancin asked: Is it possible to run the simulation at a lower temperature in order to see if the AuCu ordered phase can be obtained?

Diana Nelli responded: According to our model for the AuCu system, ordered phases are energetically favourable in crystalline fcc nanoparticles down to small sizes. We note that the ordered phase can be stabilized in the internal region of the nanoparticle, at overall nanoparticle compositions different from those of the ordered phases in bulk samples, due to the surface enrichment in Au. However, we expect that freezing simulations of a AuCu liquid droplet will not be able to produce such phases, due to the limited timescales of molecular dynamics (MD). More likely, when cooled down from the liquid, the system will solidify in solid solution configurations, in which the atoms are almost randomly intermixed, and it will remain trapped there within the MD simulation timescales.

Emmanuel Cottancin queried: Concerning the simulations on gold–copper BNPs: are the assumptions in the two simulations leading to different final structures (TO or Ih) different; if not, can we calculate the probabilities of the two final structures?

Diana Nelli replied: In our molecular dynamics simulations, the TO \rightarrow Ih transformation of AuCu nanoalloys that are 586 atoms in size is always observed at temperature $T \ge 600$ K within 10 µs, and it is never observed for $T \le 500$ K. At T = 550 K, independent simulations starting from the same structure have different outcomes, as in some cases the shape transformation takes place within 10 µs, whereas, in other cases, the nanoalloy keeps the initial fcc TO symmetry (with some defects) until the end of the simulation. We note that if one could simulate the evolution for an infinite time, the shape transformation would eventually occur in all simulations (also for temperatures lower than 550 K), because for the considered size and composition, the Ih is more energetically favourable than the TO. In this case, it is difficult to analytically estimate the probability of the TO \rightarrow Ih shape transformation within a finite timescale, such as 10 µs, due to the complexity of the transformation pathways. The only feasible strategy consists of performing several independent simulations, and calculating the probability from the occurrence rate of the two possible final structures.

Georg Daniel Förster asked: Since you have analyzed nanoalloys of different metals, what is your intuition about what are the most important driving forces determining chemical ordering? Do you think that entropic effects are important even for nanoalloys that are not considered "high entropy", such as 3-component particles?

Diana Nelli replied: The equilibrium chemical ordering of nanoalloys is determined by the interplay of different driving forces, the most important being the tendency towards intermixing (or towards phase separation) in the bulk, the surface energy difference between the two metals, and their lattice mismatch. These are also expected to be the driving forces for the lowest-energy configuration in the case of multi-component nanoparticles. However, as the number of metallic components increases, the lowest-energy configurations become less and less statistically significant, eventually leading to the thermodynamic stabilization of randomly intermixed configurations, even at low temperatures.

Hazar Guesmi commented: You show that, for Au–Cu, an icosahedral shape is more favourable than a truncated octahedron. Is it possible to get an order of the energetic stability of the two shapes?

Diana Nelli replied: For Au₄₄₆Cu₁₄₀, icosahedral (Ih) structures are more energetically favourable than truncated octahedral (TO) ones. Therefore, in our simulations, nanoparticles with an initially perfect TO shape spontaneously transform into an Ih structure if the simulation temperature is sufficiently high ($T \ge 500$ K). The shape transformation induces a sudden decrease in the potential energy of the system; the energy gain is in the range of 3–7 eV, depending on the degree of intermixing achieved when the transformation occurs. To better compare the energetic stability of the two motifs, we have performed global optimization searches using our Basin Hopping code. We have considered the perfect TO that is 586 atoms in size, and a regularly shaped Ih of the same size (*i.e.*, a perfect Ih that is 561 atoms in size, plus a surface island in anti-Mackay stacking). We have considered the same composition as in the paper (https:// doi.org/10.1039/d2fd00113f), and we have optimized the chemical ordering at a fixed geometry. According to our model, the energy difference between the best isomers of the two motifs is 3.9 eV.

Fuyi Chen communicated: The evolution of AgAu, PtPd and AuCu nanoparticles from their initial core@shell configurations to their equilibrium intermixed chemical ordering arises from a complex interplay between interdiffusion of atoms on the surface and subsurface. Will the difference between the surface and the subsurface induce some surface defects or deformations? How will the surface defects or deformations affect the structure evolution of these nanoparticles?

Diana Nelli communicated in reply: The formation of surface defects has been observed in all our molecular dynamics simulations. In truncated octahedral nanoparticles, common defects are surface islands or atomic planes in stacking faults, as also observed in monometallic nanoparticles in the same temperature range.^{1,2} In the case of bimetallic nanoparticles, such defects are even more frequent, since interdiffusion can easily induce local reshaping processes. On the other hand, in disordered regions in which atoms are poorly coordinated and/or highly strained, diffusion processes are accelerated.

¹ Y. Xia, D. Nelli, R. Ferrando, J. Yuan and Z. Y. Li, Shape control of size-selected naked platinum nanocrystals, *Nat. Commun.*, 2021, 12, 3019, DOI: 10.1038/s41467-021-23305-7.

2 E. El koraychy, C. Roncaglia, D. Nelli, M. Cerbelaud and R. Ferrando, Growth mechanisms from tetrahedral seeds to multiply twinned Au nanoparticles revealed by atomistic simulations, *Nanoscale Horiz.*, 2022, 7, 883–889, DOI: **10.1039/d1nh00599e**.

Ewald Janssens opened a general discussion of the papers by Marcelo M. Mariscal, Georg Daniel Förster and Diana Nelli: Contemporary simulations deal with kinetic effects during the growth of nanoalloys. This is important since in case of a good understanding and control, out-of-equilibrium growth can be used to make unique nanoalloy morphologies. One issue for the comparison of simulations with experiments is the time gap. While experimental timescales are, depending on the experimental approach, in the range of microseconds to seconds, simulations usually deal with much shorter timescales (picoseconds to microseconds). In molecular dynamics, often a higher temperature is used to speed up the dynamics. How trustworthy is this approach?

Marcelo M. Mariscal answered: Raising the temperature could be a first "not elegant" solution. In my opinion, the best way should be accelerated dynamics methods, *i.e.*, temperature-accelerated dynamics, hyperdynamics, and so on.

Georg Daniel Förster answered: The reason for this approach is that the cost of computing molecular dynamics on experimental timescales is excessive. As long as the Arrhenius equation is a good approximation, the approach should give reasonable results. The problem, however, is that the energy landscape and associated barriers are temperature dependent, which unfortunately limits the reliability of the results. If the growth conditions are not too far from thermo-dynamic equilibrium, the approximation can be considered justified if the higher temperature keeps the growth pathways close to equilibrium, albeit at an increased temperature. However, this is not always the case.

Diana Nelli responded: In recent years, the timescales achievable by atomistic molecular dynamics (MD) simulations have largely increased. To date, it is possible to simulate the evolution of nanoparticles of several thousands of atoms for several tens of microseconds, thus approaching the typical timescales of nanoparticle formation in the gas phase. However, experimental timescales can be much longer. In these cases, a direct quantitative comparison between experimental and MD results is not feasible; anyway, MD simulations can still provide useful insights to better interpret the experimental data. Raising the simulation temperature is indeed a common approach to speed up the evolution of the system, in order to observe significant changes within the limited simulation time. Though it does not strictly correspond to extending the timescale, this approach makes it possible to observe different possible evolution pathways, thus improving the knowledge of the system dynamics. In this respect, multiple MD simulations at different temperatures are needed. We note that more sophisticated simulation techniques can be used to accelerate the dynamics at room temperature; however, these approaches often require a good knowledge of the systems, and make use of some assumptions on its evolution pathways. Once again, such information can be obtained by preliminary high-temperature MD simulations (see, for example, ref. 1).

¹ D. Nelli, F. Pietrucci and R. Ferrando, Impurity diffusion in magic-size icosahedral clusters, *J. Chem. Phys.*, 2021, **155**, 144304, DOI: **10.1063/5.0060236**.

Francesca Baletto addressed all: We heard about reconstructions and chemical reordering due to temperature, stress, pulling forces, and effects of the substrate. Eventually we need to better clarify and understand when and how those morphological changes are collective or when they proceed throughout individual atomic processes. This might help in understanding their intrinsic timescale.

I believe that we need to comment on the choice of the interparticle potential, in terms of its accuracy. It might be that a qualitative description is enough to predict the timescale of structural and chemical transformations, but a proof is needed.

Georg Daniel Förster responded: Thank you for your comment, I absolutely agree.

Diana Nelli added: The results of our molecular dynamics simulations and of other simulations in the literature show that collective processes are by far the most dominant in the evolution of the shape and chemical ordering of nanoalloys. We have observed collective processes for several different mono- and bimetallic systems, in a wide range of sizes and temperatures, including room temperature. We believe that this qualitative trend is reflecting the real behaviour of the systems. Of course, quantitative accuracy depends on the reliability of the atomic interaction model, and should be checked for each system, if possible.

Swathi Swaminathan addressed Georg Daniel Förster and Diana Nelli: In cobalt–silver and gold–silver nanoparticle experimental synthesis, we observe oxidized species (like Ag^+ or Co^{2+}) on exposure to air. Do you introduce any charges when modelling their formation in your simulations?

Georg Daniel Förster answered: We simulated particle growth in a vacuum and did not attempt to account for potential oxidation. Nevertheless, I agree with you that it may be an important factor to consider in ambient conditions. Oxidation can in principle be simulated, but requires specialized modelling, which considerably increases computational cost.

Nanoalloy catalysis, part 1

Alessandro Fortunelli opened a discussion of the paper by Štefan Vajda: Nice work, clearly showing the influence of the support on the catalytic activity of subnanometer clusters. In this respect, did you correlate the influence of the support with some physico-chemical properties, such as acidity/basicity; concepts used in the literature to rationalize the activity of oxide supports, not only as catalysts but also as supports?

A related property may be the hydroxylation state of these oxide supports.

Štefan Vajda replied: We have not made such systematic correlations yet and agree that the level of hydroxylation of the support is one of the properties of the support with a potentially pronounced effect on performance.

Joost M. Bakker said: Given the size of the deposited clusters studied here, I could imagine the reaction between these clusters and cyclohexene has been studied in the gas phase and/or with density functional theory. Such studies, and, in particular, studies involving clusters with different charge states may shed light on the support effects you observe, potentially in terms of charge donation by the support. Are you aware of any of these?

Štefan Vajda responded: I am not aware of gas-phase studies of this reaction on free clusters with different charge states. Such complementary studies could provide important insights into the effect of charge/charge transfer between the support and the cluster, an effect that is significantly more pronounced for ultrasmall clusters than large particles. An interesting example is atomic silver clusters, which in the gas phase can activate oxygen molecules at cryogenic temperatures if the clusters are negatively charged.

Graham J. Hutchings commented: You report 100% selectivity for benzene (https://doi.org/10.1039/d2fd00108j), which is very interesting. What is the reason for this complete specificity? Is it because benzene is not oxidised on this catalyst or is it because benzene competes very successfully with oxygen, thereby stopping the overoxidation?

Stefan Vajda responded: Based on available data, we cannot distinguish the roots of this high selectivity. Additional experiments, such as studies of dehydrogenation at variable cyclohexene to oxygen ratios and/or studies of the oxidation of benzene by these catalysts, may provide the answer.

Ewald Janssens remarked: In your experiments, you have very good control over the size and composition of the clusters, but not over the structure of the clusters on the surface. There may be different binding sites and structural isomers. Are you aware of any examples in your research where the reactivity is dominated by a minority species (higher-energy isomers or energetically less favorable binding sites)?

Štefan Vajda answered: The clusters are not rigid structures. In addition to the variety of possible structural isomers they may possess upon deposition, the clusters can undergo restructuring during the course of the reaction as well. The reaction rates obtained reflect the activity of the entire ensemble. Based on available data, we are not in the position to distinguish whether there is a dominance by one isomer or another.

Swathi Swaminathan asked: What is the fate of the hydrogen following the dehydrogenation? Is it leaving as H₂? Have you looked at the by-products of your reaction?

Štefan Vajda answered: Under oxidative conditions we expect that hydrogen will be removed primarily in the form of water. We monitor the formation of possible byproducts by operating the mass spectrometer in a mass-scanning mode and the identified species are discussed in the paper. Water formation is seen in the experiment. While we cannot fully exclude that some fraction of

hydrogen leaves in the form of H_2 , we have no experimental proof of it – such could be gained using gas chromatography, for example.

Pinkie Ntola communicated: What phase of the TiO₂ was this (rutile/anatase or a mixture)? How does it compare to the other phases in performance?

Štefan Vajda communicated in reply: The thin oxide films used in the study (https://doi.org/10.1039/d2fd00108j) were prepared by atomic layer deposition, which yields amorphous films.

Fuyi Chen communicated: $Cu_{4-n}Pd_n$ tetramer clusters may be oxidized under high-temperature reaction conditions. Does oxidation of the catalyst affect the activity and selectivity?

Štefan Vajda communicated in reply: Yes, the oxidation state of a catalyst can, in general, affect both activity and selectivity. The studies presented in this particular paper (https://doi.org/10.1039/d2fd00108j) did not include *in situ* characterization, thus we cannot comment on the oxidation state in this case.

Hans-Christian Weissker opened a discussion of the paper by Noelia Barrabés: We know that the monolayer-protected clusters can be "atomically precise" and their geometry in many cases known. When you apply co-doping or alloying, how much does that influence the geometry and, maybe, the size dispersion?

Noelia Barrabés answered: Several groups have used XAFS spectroscopy to demonstrate that the structure does not exhibit strong distortions upon doping.

Lebohang Macheli queried: What differences do different solvents bring to the clusters that affect their overall performance?

Noelia Barrabés responded: If I understood the question correctly, the solvents during the synthesis represent a protocol variable. The synthesis is a chemical reaction where the kinetics are also affected by the solvent properties. Different solvents are used depending on the size range you want to produce. However, we do not develop the synthesis, but only use the methods already reported for these types of clusters, all based on the Brust method.

John McGrady remarked: In the paper (https://doi.org/10.1039/d2fd00120a), you make a very clear distinction between Co^+ and Au^{δ^+} . Can you comment on the basis for this – is the partial charge on Au based on population analysis, for example? Does the difference in charges tell us something important about the nature of the interaction between the surface and the substrate?

Noelia Barrabés replied: The Au^{δ^+} represents a partially-charged state and it was assigned based on CO-FTIR studies, analyzing the vibration band of the CO on Au, and in agreement with XPS. CO-FTIR was also used to study the charge state of cobalt; as with XPS and XAFS, no clear results were obtained (due to the low amount of cobalt in the sample). The Co⁺ results clarify the strong interaction between Au and Co leading to the alloy sites. The interaction with the support is

expected with the Au atoms, even with some S atoms from the staple motif, but the interaction with some Co atoms located on the Au core structure cannot be excluded.

Alessandro Fortunelli commented: Nice work. In the interpretation of the EXAFS synchrotron experiment, do you use atomistic configurations for the clusters taken from X-ray crystal data? Would you expect that there are differences in the arrangements of atoms due to the interaction with the substrate?

Noelia Barrabés responded: Yes, the crystal structures for the clusters are used to fit the EXAFS spectra. The interaction with the support leads to a strong interaction mainly with the staple motifs and ligands around the cluster core. During pretreatment, these systems have some dynamics leading to migration to the surface, but only with respect to the ligand/staple interface, not with respect to the cluster core structure. We have studied the dynamics of the supported monometallic and other bimetallic clusters in previous publications.^{1–4}

- 1 V. Truttmann, H. Drexler, M. Stöger-Pollach, T. Kawawaki, Y. Negishi, N. Barrabés and G. Rupprechter, CeO₂ Supported Gold Nanocluster Catalysts for CO Oxidation: Surface Evolution Influenced by the Ligand Shell, *ChemCatChem*, 2022, **14**, e202200322, DOI: **10.1002/cctc.202200322**.
- 2 B. Zhang, A. Sels, G. Salassa, S. Pollitt, V. Truttmann, C. Rameshan, J. Llorca, W. Olszewski, G. Rupprechter, T. Bürgi and N. Barrabés, Ligand Migration from Cluster to Support: A Crucial Factor for Catalysis by Thiolate-protected Gold Clusters, *ChemCatChem*, 2018, 10, 5372–5376, DOI: 10.1002/cctc.201801474.
- 3 S. Pollitt, V. Truttmann, T. Haunold, C. Garcia, W. Olszewski, J. Llorca, N. Barrabés and G. Rupprechter, The Dynamic Structure of Au₃₈(SR)₂₄ Nanoclusters Supported on CeO₂ upon Pretreatment and CO Oxidation, *ACS Catal.*, 2020, **10**, 6144–6148, DOI: **10.1021**/**acscatal.0c01621**.
- 4 C. Garcia, V. Truttmann, I. Lopez, T. Haunold, C. Marini, C. Rameshan, E. Pittenauer, P. Kregsamer, K. Dobrezberger, M. Stöger-Pollach, N. Barrabés and G. Rupprechter, Dynamics of Pd Dopant Atoms inside Au Nanoclusters during Catalytic CO Oxidation, *J. Phys. Chem. C*, 2020, **124**, 23626–23636, DOI: **10.1021/acs.jpcc.0c05735**.

Pascal Andreazza asked: How do you evaluate the size and size evolution of the cluster? Is it only determined from the nearest neighbour (NN) numbers obtained by EXAFS? In addition, for the initial Au₂₅ and Co-doped Au₂₅ clusters in various solvents characterized by EXAFS, you showed in Fig. 2 of your paper (https://doi.org/10.1039/d2fd00120a) very unexpected NN number variations (total number and NN number for each neighbour type). Could you explain these variations?

Noelia Barrabés replied: We did not evaluate the cluster size. Since the XAS experiment looks at the whole sample, the fit only tells us the average coordination number. So, atoms inside the cluster contribute more to this number than the ones on the surface. The different shapes of the second peak in the FT (marked in violet in Fig. 2 of our paper (https://doi.org/10.1039/d2fd00120a)) could be due to variations in the cluster size, and some variation should be expected. The variation will be related to the dynamics of the Co atoms inside the cluster, ligand removal and a slight increase in the particle size.

Éric Marceau commented: In the EXAFS fits, the Au–Co distance varies between 2.69 and 2.89 Å, which is quite a large interval, and, in the unsupported nanoparticles, the Debye–Waller (DW) parameter for the Au neighbours happens to be very large. How do you interpret it?

Didier Grandjean added: I have noticed that, in the EXAFS fit results presented for Au₂₅ in Fig. 2 of your paper (https://doi.org/10.1039/d2fd00120a), the Debye– Waller factor σ^2 associated with the Au–Au shell is 0.001, which is abnormally small (0.01–0.02 should be expected). As this factor is correlated with the coordination number, could you check the fit again?

Noelia Barrabés replied: The fittings were checked and confirmed.

The coordination number and DW factor are correlated. But not only this. Additionally, in the systems with asymmetries in coordination spheres (as for the cluster), correlations between distances and DW factors are not negligible. They may cause instabilities in the fitting process resulting in physically unreasonable parameter values (coordination numbers, DW factors, and distances). Usually the further coordination spheres are more severely affected by this problem (since we are trying to fit one broad peak with two contributions close to each other – see Fig. 4 with fitting paths). But it may happen in the first coordination sphere as well.

(i) To do the fits of the Au_{25} cluster, we used the reported crystallography data. The fitting procedure started with the coordination number given in this file. Results of DW factors in the range of 0.001–0.002 are not strange for the crystal structures. (ii) DW factors for all the Au–Au pairs (except for the Au_{25} cluster) are quite similar, around 0.01–0.02. As for the distance, the variations can be a result of the correlation problem that could be related to a slight increase in the particle size, which is already expected and observed in previous works.¹

1 C. Garcia, V. Truttmann, I. Lopez, T. Haunold, C. Marini, C. Rameshan, E. Pittenauer, P. Kregsamer, K. Dobrezberger, M. Stöger-Pollach, N. Barrabés and G. Rupprechter, *J. Phys. Chem. C*, 2020, **124**, 23626–23636.



Rolf Schäfer asked: What happens to the ligands during CO oxidation?

Fig. 4 FEFF calculation.

Noelia Barrabés replied: The ligands are removed during the pretreatment before the reaction. If some ligands remain in the cluster, they will be further removed during CO oxidation.

Michael Bowker queried: Can you tell us how Co alone behaves, compared with Au and the alloys?

Noelia Barrabés answered: We also prepared Co nanoclusters, which were tested in the reaction leading to really low activity and deactivation of the catalyst. The alloys of the Co atoms inside the Au clusters were stabilized and had an enhanced reactivity.

Christian Kuttner commented: For someone who has never worked with atomic clusters, the UV-Vis data of the Co-doped Au_{25} clusters seem very difficult to analyze. Could you explain what information can be drawn from the optical spectra and how the variability of the co-doping sites is reflected in the spectra?

Noelia Barrabés responded: The optical activity (UV-Vis spectra) is related to the electronic structure of the cluster, which also depends on the structure. Therefore, the UV-Vis spectrum represents the fingerprint of the particular cluster structure. For example, in the case of $Au_{25}(PET)_{18}$ clusters, the characteristic peaks are related to the transition from the highest occupied orbitals (HOMOs) to the lowest unoccupied orbitals (LUMOs). When one or more Au atoms are replaced by another metal atom, there is a change in the LUMOs (depending on their position), which leads to a shift and broadening of the characteristic UV-Vis peaks. The UV-Vis spectrum is also calculated from the cluster structure and also helps in interpretation.

Jonathan Quinson commented: If I understand right, you did not try to remove the thiols on the as-prepared samples (before you performed the heat treatment). On the as-produced nanoparticles, I am wondering if you see any effect of the cobalt content on the thiol "shell", *e.g.*, a shift in infrared, or XPS, or hydrodynamic radius, or maybe on the amount of ligand from TGA? In other words, does the doping change the way the thiols interact with the surface? You mentioned previous work of yours in this direction and I would like to be directed to it. Did that work include bimetallic clusters? Thanks.

Noelia Barrabés responded: Previous work has been done with bimetallic Pdand Ag-doped Au_{25} clusters.^{1,2} It was observed that when the doped atoms are located in the center of the Au cluster, the Pd atoms migrate to the surface of the core after pretreatment. On the other hand, in the case of Ag in the staple and surface, which is similar to that of Co, the doped atoms also migrate into the Au core structure during pretreatment and form alloy sites.

C. Garcia, V. Truttmann, I. Lopez, T. Haunold, C. Marini, C. Rameshan, E. Pittenauer, P. Kregsamer, K. Dobrezberger, M. Stöger-Pollach, N. Barrabés and G. Rupprechter, Dynamics of Pd Dopant Atoms inside Au Nanoclusters during Catalytic CO Oxidation, *J. Phys. Chem. C*, 2020, **124**, 23626–23636, DOI: **10.1021/acs.jpcc.0c05735**.

² I. López-Hernández, V. Truttmann, C. Garcia, C. W. Lopes, C. Rameshan, M. Stöger-Pollach, N. Barrabés, G. Rupprechter, F. Rey and A. E. Palomares, AgAu nanoclusters

supported on zeolites: Structural dynamics during CO oxidation, *Catal. Today*, 2022, **384**–**386**, 166–176, DOI: **10.1016/j.cattod.2021.04.016**.

Christian Kuttner asked: Can one assume that the Co atoms migrate to the surface of the Au core during pretreatment?

Noelia Barrabés responded: Indeed, some Co atoms might already be on the Au core and others in the staples that migrate into the Au core structure during pretreatment. We have observed similar behavior in previous studies with Pd- and Ag-doped Au clusters.

Fuyi Chen communicated: A AuCo alloy was successfully prepared and exhibited better CO oxidation performance than monoelement Au when the CO oxidation reaction on the alloy was studied dynamically. As the spectral evolution in Fig. 5 of your paper (https://doi.org/10.1039/d2fd00120a) shows, the enhanced CO oxidation property is related to the presence of Co⁺ for all the alloy samples. The question is, why is it Co⁺ instead of Co⁰, since the Co atoms are confirmed within the cluster. If monovalent Co is derived from oxidative pretreatment, what is the effect of O₂ pretreatment and what is the purpose of O₂ pretreatment?

Noelia Barrabés communicated in reply: The O_2 pretreatment is expected to remove the thiolated ligands around the cluster metal core structure. Once the ligands are removed, an alloy forms between the Co and Au atoms at the surface of the cluster core, which explains why it is not in the metallic state.

Mzamo Shozi communicated: (a) In the synthesis of the catalysts, could one use diethyl ether instead if they wanted to avoid a chlorinated solvent like DCM? (b) Would water work as a solvent for this synthesis?

Noelia Barrabés communicated in reply: Solvents used in the synthesis of nanoclusters include DCM, THF or MeOH. If you only want to prepare water-soluble clusters (depending on the type of ligand), you can work with water. We have no experience with diethyl ether.

Conflicts of interest

There are no conflicts to declare.