

Theory as a driving force to understand reactions on nanoparticles: general discussion

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DOI: 10.1039/C8FD90013B

Carlo Lamberti opened discussion of the introductory lecture by Bruce Gates: As you have shown, EXAFS plays a crucial role in determining the structure and the nuclearity of nanoparticles (NPs). For each shell, the accuracy of this determination depends on the error bar associated to the coordination number, that strongly correlates with the corresponding Debye–Waller (DW) parameter. This becomes even more important when *in situ operando* experiments are performed at reaction temperature. Based on your experience, what suggestions can you give to reduce this correlation and increase the potentiality of the technique? Do you believe it is possible to fix or to determine, in a reliable way, DW parameters from independent experimental or computational works? Do you believe that in temperature-dependent experiments it is reliable to adopt the Debye or the Einstein model^{1,2} to parametrize the evolution of DW parameters?

1 G. Dalba, P. Fornasini, R. Grisenti and J. Purans, *Phys. Rev. Lett.*, 1999, **82**, 4240–4243.

2 S. Øien, G. Agostini, S. Svelle, E. Borfecchia, K. A. Lomachenko, L. Mino, E. Gallo, S. Bordiga, U. Olsbye, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2015, **27**, 1042–1056.

Bruce Gates answered: You raise good points, and all I would like to state is that it is valuable to have corroborating evidence from other techniques to determine the coordination number. For example, triosmium clusters on a support, if synthesized with high precision, can be characterized by STEM to determine the cluster nuclearity (hence the Os–Os coordination number) for

comparison with the EXAFS value. Furthermore, IR spectra of triosmium carbonyls provide evidence of the structure (including the cluster nuclearity). Insofar as such comparisons have been made, for various osmium clusters on supports, the data confirm the Os–Os coordination number determined by EXAFS spectroscopy. See, for example, ref. 1–3. Perhaps samples such as these can be used in experimentation to address the questions you have raised.

- 1 N. L. Okamoto, B. W. Reed, S. Mehraeen, A. Kulkarni, D. G. Morgan, B. C. Gates and N. D. Browning, Determination of Nanocluster Sizes from Dark-Field Scanning Transmission Electron Microscopy Images, *J. Phys. Chem. C*, 2008, **112**, 1759.
- 2 A. Kulkarni, S. Mehraeen, B. W. Reed, N. L. Okamoto, N. D. Browning and B. C. Gates, Nearly Uniform Decaosmium Clusters Supported on MgO: Characterization by X-ray Absorption Spectroscopy and Scanning Transmission Electron Microscopy, *J. Phys. Chem. C*, 2009, **113**, 13377.
- 3 S. Mehraeen, A. Kulkarni, M. Chi, B. W. Reed, N. L. Okamoto, N. D. Browning and B. C. Gates, Triosmium Clusters on a Support: Determination of Structure by X-Ray Absorption Spectroscopy and High-Resolution Microscopy, *Chem.–Eur. J.*, 2011, **17**, 1000.

Rutger van Santen said: You mentioned the unique stability of cubic Ir nanoparticles of particular size. Do the total number of atoms in these particles agree with the ideal structures? Can one exclude the possibility that the presence of particular surface edge features or surface reconstruction, that is only stable when a particular surface size is reached, are the explanations?

Bruce Gates responded: The TEM images show a range of sizes of Ir species, ranging from the single-atom complexes to the nanoparticles that are all about 1 nm in diameter or less. The images indicate various nanoparticle morphologies, and one that was emphasized in the presentation is evidently cubic. Whether the distribution of nanoparticles evolves to cubic nanoparticles after long times is not determined by the data. Neither the experimental results nor the theory of Pawlik *et al.* (ref. 51 in the paper) exclude the possibilities you have suggested.

Justin Hargreaves asked: Taking the analogy with organometallic chemistry further, to what extent is it possible to produce an empirical ranking of supports in terms of some parameter akin to the Tolman electronic parameter?

Bruce Gates replied: The expectations one would have on the basis of organometallic catalysis in solution, in my view, extend seamlessly to supported metal complex (and, presumably, metal cluster) catalysts when they have a high degree of uniformity. For example, ref. 1 reported correlations of the activities of supported mononuclear iridium complexes (measured as turnover frequencies) for ethylene hydrogenation and for ethylene dimerization with the carbonyl stretching frequencies of the iridium complexes in the catalysts after they were exposed to CO to form anchored iridium *gem*-dicarbonyls. These frequencies are a measure of the electron-donor tendency of the supports, which are ligands. Thus, the correlations provide the kind of empirical ranking that you are referring to, and they represent a family of supports, some being electron donating and some being electron withdrawing, and account for orders of magnitude ranges in the catalytic activities. It is important in this context that the supported catalysts are not highly non-uniform on the supports and thus nearly unique (and essentially molecular).

1 D. Yang, S. O. Odoh, T. C. Wang, O. K. Farha, J. T. Hupp, C. J. Cramer, L. Gagliardi and B. C. Gates, *J. Am. Chem. Soc.*, 2015, **137**, 7391–7396.

Kassim Badmus commented: Why does a zeolite not give consistent result in its characterization and when it is used as a support? Can you tell us the factors that must be considered before we choose a support for a nanoparticle? Can the pore size be responsible for the inconsistency in characterization of zeolite systems?

Bruce Gates replied: For a given zeolite sample, our data show good reproducibility. But zeolite syntheses give samples with variable compositions (distributions of Si and Al sites) and the initially formed crystals of a zeolite generally don't match the ones formed later in a batch synthesis; furthermore, synthesis of many zeolites is challenging to reproduce. Some syntheses give more than one zeolite, and some samples of zeolites incorporate amorphous material. In general, in finding porous supports (zeolites or others) for metal nanoparticle catalysts, one must consider the support surface chemistry, because it influences the synthesis of the supported species, and the pore size distribution, because mass transfer of reactants and products in the pores can affect rates of catalytic reactions (and blocking of small pores by the nanoparticles can occur).

Maurits Boeije asked: Based on your previous work,¹ can you draw the general conclusion that partially encapsulated nanoparticles in a matrix can improve stability of a catalyst by restricting nanoparticle motion and preventing coalescence?

1 J. Zhang, L. Wang, Y. Shao, Y. Wang, B. C. Gates and F.-S. Xiao, *Angew. Chem., Int. Ed.*, 2017, **56**, 9628.

Bruce Gates answered: With proper preparation, zeolite-encapsulated nanoparticles of various metals can indeed be stabilized against sintering and coke formation; details are to be published soon; see ref. 48 of the paper.

Carlo Lamberti asked: Based on your experience, do you believe that EXAFS is able to discriminate among metal–carbon, metal–oxygen and metal–nitrogen bonds? Do you believe that the recent experimental and theoretical progress of X-ray Emission spectroscopy (XES)^{1,2} will promote the technique as a standard characterization tool in the near future? Recently XES has been able to discriminate between first-shell Cu–O and Cu–N bonds in Cu–CHA catalyst during NH₃-assisted selective catalytic reduction of NO_x.^{3,4} In this regard, XES even succeeded in the discrimination between Al and P in the second shell environment of Ti–AlPO-5 catalyst.⁵ An exhaustive understanding of the XES spectra however requires the theoretical support of DFT calculations.^{6,7}

1 P. Glatzel and U. Bergmann, *Coord. Chem. Rev.*, 2005, **249**, 65–95.

2 J. Singh, C. Lamberti and J. A. van Bokhoven, *Chem. Soc. Rev.*, 2010, **39**, 4754–4766.

3 F. Giordanino, E. Borfecchia, K. A. Lomachenko, A. Lazzarini, G. Agostini, E. Gallo, A. V. Soldatov, P. Beato, S. Bordiga and C. Lamberti, *J. Phys. Chem. Lett.*, 2014, **5**, 1552–1559.

4 K. A. Lomachenko, E. Borfecchia, C. Negri, G. Berlier, C. Lamberti, P. Beato, H. Falsig and S. Bordiga, *J. Am. Chem. Soc.*, 2016, **138**, 12025–12028.

5 E. Gallo, A. Piovano, C. Marini, O. Mathon, S. Pascarelli, P. Glatzel, C. Lamberti and G. Berlier, *J. Phys. Chem. C*, 2014, **118**, 11745–11751.

always easy to do; in part because it can be challenging (especially when the relevant conditions involve complex feedstocks, high pressures, and high temperatures) to apply the methods to ensure that they all provide characterization of the same catalyst. In principle, the more such methods can be applied the better, and it is advantageous when all the measurements are done with the same apparatus – optimally, in my view, this prospect would allow measurement of vibrational spectra, X-ray absorption spectra, images, and more, along with catalyst performance data. This is in my opinion an essential question and can help motivate advances in the characterization methods.

Philip Davies opened the discussion of the paper by Rutger van Santen: In your very interesting paper you highlight the difficulties of building accurate kinetic models of catalytic systems. What, in your view, are the experimental advances needed to provide the data necessary to make calculations more realistic?

Rutger van Santen responded: Reliability of the microkinetics simulated predictions is improved by validation of the supporting quantum-chemically calculated elementary reaction rates by experiments that focus on a comparison of such rates measured at a molecular level rather than comparison with macroscopic kinetics. Agreement with the latter is never a guarantee that the predicted mechanism of the reaction is actually correct, because kinetics will lump the molecular information together.

Richard Catlow commented: One general issue that needs to be considered when discussing the interplay between theory and experiment is often the state of the catalysts is not well defined making detailed comparisons difficult. This problem needs to be addressed by a joint computational–experimental approach.

Cynthia Friend responded: I wholeheartedly agree.

Bruce Gates said: I concur and would emphasize that comparisons of experiment with theoretical predictions of supported catalysts can be especially fruitful when the supported species are synthesized precisely to give samples that have a high degree of uniformity, and there are now some examples showing good agreement between theory and experiment and opportunities for further work in this direction. For some recent examples, see ref. 1.

1 B. C. Gates, M. Flytzani-Stephanopoulos, D. A. Dixon and A. Katz, Atomically dispersed supported metal catalysts: perspectives and suggestions for future research, *Catal. Sci. Technol.*, 2017, 7, 4259

Katerina Soulantica stated: I strongly agree with this comment and I am persuaded that synthetic protocols which reproducibly afford a variety of real-catalysts with the specific characteristics predicted to be necessary from modeling and mechanistic studies on model systems, are a prerequisite. The standard existing procedures for real-catalyst preparation are not well adapted for such a high degree of control. The best catalyst configuration may correspond to a real synthetic challenge, but several procedures of well-defined nanoparticles are already available and this is a good starting point. I believe that in the future

we could think about creating a library of benchmark synthetic procedures in parallel to benchmark modeling techniques in order to be able to make the optimal calculated catalyst as predicted from theory and *in situ* measurements a reality.

Rutger van Santen commented: Yes, I completely agree. Methods are available to study surface reconstruction, using molecular dynamics or equilibrium approaches that establish the state of a surface in equilibrium with a reactant medium. It may even be necessary to consider the transition between different surface states when reactions are oscillatory. For not too complex reactions (oxidation of CO by transition metals or oxides) kinetic Monte Carlo simulations are available that demonstrate this computationally. However the timescales of surface reconstruction (sometimes activated and slow) will usually not match the timescale of the catalytic reaction cycle and then the two have to be simulated independently. There is usually very limited information on the state of the working catalyst under practical conditions. The latter is essential because it often sensitively depends on conditions (the pressure, temperature gap). Such measurements will help to validate kinetics simulations.

Keith Whiston asked: Is it possible using your microkinetic modelling approach to incorporate aspects of zeolite geometry as predictors within the model? Either by using them to represent the Brønsted acidic properties of the catalysts and also to predict the effects of diffusion on product distribution and deactivation rate?

Rutger van Santen answered: One property that is very sensitive to zeolite pore geometry is the adsorption isotherm of hydrocarbons. There is a very approximate relation between matching molecular size and cavity shape. But there are methods, such as the Configurational-Bias Monte Carlo (CB-MC) method, that provide the relevant numbers directly.

The case of diffusion is more complicated. Knudsen diffusion does not apply to zeolites, since diffusion in zeolites is of the ballistic type. Also for this case excellent molecular dynamics approaches are available to estimate the corresponding diffusion constants. If one would like to define predictors, they relate again to a match between molecule shape and volume with that of the microcavity.

A Monte Carlo approach would enable the inclusion of diffusion in the kinetics modelling. This implies definition of size of crystallite and explicit consideration of zeolite nanopore topology. Since the diffusion of the small reactant molecules we consider is fast compared to reaction rate, we did not include diffusion explicitly in our microkinetics modelling.

The effect of varying proton acidity, assuming that zeolite structure remains the same, can be readily incorporated in the microkinetics simulations by varying the activation energies of the elementary reaction steps using the BEP linear activation energy–reaction energy relationships, that are valid as long as the structure of the reaction intermediates does not vary. A probe of the proton reactivity is its bond strength, which can be measured in several ways.

Francesca Baletto asked: Could you provide more information on the importance of site reconstruction and comment whether the lattice mobility should be included into a microkinetic model?

Rutger van Santen answered: Especially in transition metal catalysis the phenomenon of site reconstruction when the catalyst is exposed to a reactive medium is quite general. In order to actually determine the structure and composition of the surface overlayer that forms, displacement of the lattice atoms has to be taken into account. However the timescale of a catalytic reaction cycle is such that on that timescale the reaction can usually be assumed to take place on a surface where the transition atom mobility is slow. Then the determination of the surface structure and composition can be done independently once an overlayer concentration of adatoms has been established.

This however is not generally the case. Exceptions are surface reactions that self-organize, as the Ertl-related systems and systems where a liquid overlayer forms, as is most likely the case in oxychloride systems.

Carlo Lamberti said: Concerning the machine learning (ML) approach, it is worth mentioning the recent work of Frenkel and co-workers,¹ which has shown that the size, shape and morphology of Pt nanoparticles (NPs) can be obtained from XANES spectroscopy supported by a ML approach. The ML method was trained with *ab initio* XANES simulations on a huge library of clusters. Consistent results were obtained simulating the spectra with both FEFF-9² and FDMNES³ codes, resulting in the correct 3D reconstruction of the NPs. On the other hand, a library of XANES spectra for Pd hydrate and Pd carbide phases has been created, on DFT-optimized geometries, changing the Pd–Pd distance and the *x* and *y* stoichiometries of the PdH_{*x*} or PdC_{*y*} phases (ref. 4 and DOI: 10.1039/c7fd00211d) This allowed the authors to determine both structure and composition of Pd NPs under hydrogenation reactions. These kinds of studies demonstrated that XANES spectroscopy can be applied for high-throughput, time-dependent, studies typical of *operando* investigation of a catalytic system.

- 1 J. Timoshenko, D. Lu, Y. Lin and A. I. Frenkel, *J. Phys. Chem. Lett.*, 2017, **8**, 5091–5098.
- 2 J. J. Rehr, J. J. Kas, F. D. Vila, M. P. Prange and K. Jorissen, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5503–5513.
- 3 S. A. Guda, A. A. Guda, M. A. Soldatov, K. A. Lomachenko, A. L. Bugaev, C. Lamberti, W. Gawelda, C. Bressler, G. Smolentsev, A. V. Soldatov and Y. Joly, *J. Chem. Theory Comput.*, 2015, **11**, 4512–4521.
- 4 A. L. Bugaev, O. A. Usoltsev, A. A. Guda, K. A. Lomachenko, I. A. Pankin, Y. V. Rusalev, H. Emerich, E. Groppo, R. Pellegrini, A. V. Soldatov, J. A. van Bokhoven and C. Lamberti, *J. Phys. Chem. C*, 2018, **122**, 12029–12037.

Bruce Gates replied: I would add the thought that further progress in this direction might be facilitated by work with structurally well-defined and nearly uniform supported species and not just samples such as those of Frenkel *et al.* that consist of a smear of structures.

Yaroslav Odarchenko said: Thank you very much for your talk. Our group is also studying the deactivation mechanism of the FTS catalyst. In your paper you discuss only the promotional effect of water. However, in our experimental work

on Co-based catalyst¹ we have observed that metal nanoparticles oxidize most probably due to the presence of water. What are your thoughts about this?

1 P. Senecal *et al.*, *ACS Catal.*, 2017, 7, 2284–2293.

Rutger van Santen replied: This is a well known phenomenon that is observed for many transition metal particles when on the nanoscale. It will be a strong function of particle size. In Fischer–Tropsch catalysis it has been a long open question whether the deactivation of the catalyst for Co particles less than 6 nm in size is due to oxidation or intrinsic. The consensus now is that this deactivation is an intrinsic property of the small particles.

Cynthia Friend opened the discussion of the paper by Roy Johnston: Because your motivation for studying these systems was hydrogenation reactions, the titania support will be partially reduced under catalytic conditions. Prior work has shown that this leads to overgrowth of metal nanoparticles, including Rh (so-called strong metal support interactions (SMSI)). Did you consider such changes? If not, how would you approach this using theory? What methodology is required?

Roy Johnston answered: No we have not considered partial reduction of the titania support, though I agree this will be important in a future study of hydrogenation on AuRh catalysts. There should not be too much of a problem actually carrying out these calculations, though we would probably have to use a larger surface cell, so they will be more computationally expensive. However, generating configurations with overgrowth of partially reduced titania maybe more of a problem. In the absence of reliable empirical potentials to describe all of the required interactions, it may be necessary to carry out short DFT molecular dynamics simulations.

Aram Bugaev asked: Have you considered the effect of the thickness of the support on the bonding energies and geometries?

Roy Johnston answered: For the titania support we tested the convergence of the energy with the slab thickness. Reasonable convergence (when balanced against computational cost) was found for a slab of three TiO₂ (110) layers, corresponding to 9 layers of atoms. When calculating the surface binding energies of the AuRh and PdIr nanoparticles, the bottom TiO₂ layer was kept fixed, to mimic bulk TiO₂, and the top two layers were allowed to relax. However, we have not investigated how the cluster surface binding energy or geometry depends on the slab thickness. This is a good idea for a future study.

Hans-Joachim Freund queried: Have you considered charge transfer as a function of the distribution of Au and Rh with respect to the distance to the surface and in particular how that would be influenced by defects on the surface of TiO₂ or even below the surface.

Roy Johnston answered: No we have not investigated these aspects of charge transfer, but I agree that this would be a useful future study.

preferential CO oxidation, both CO and oxygen adsorbed on the catalysts can change the surface composition due to selective segregation of one of the elements.

Roy Johnston answered: Although we have not yet investigated thermal effects, for the 38-atom AuRh particles we found that the greater adsorption energies of CO and O₂ to Rh (as compared to Au) means that (in the presence of these molecules) configurations with some degree of Rh migration to the surface are lower in energy than the Rh@Au core-shell structure (ref. 23 in the paper).

Graham Hutchings remarked: The method of preparation you have used for your supported bimetallic nanoparticles is an impregnation technique and will produce atoms, clusters and nanoparticles which are evident in your micrographs. Do the clusters contain both metals? Or is there a minimum cluster size at which the second metal can be included or become stable? For some reaction such bimetallic clusters could be very effective and so accessing such structures could be useful if such structures can be readily made.

Roy Johnston replied: I believe that most of the clusters contain both elements. After heat treatment (700 °C) of the AuRh system, some pure Au and Rh NPs are indeed observed, in addition to Janus AuRh particles, with predominantly Rh at the nanoparticle-TiO₂ interface.¹ Since there is some degree of Au overgrowth at the edges of the Rh sub-clusters, these can be described as “ball-cup” configurations.

1 L. Piccolo *et al.*, *Sci. Rep.*, 2016, **6**, 35226.

Chris-Kriton Skylaris asked: Have you included or examined including thermal effects in your calculations of binding of metal nanoparticles to titania? As they stand, binding energies are computed at 0 K while we know that in real applications we have finite temperatures and the binding is determined by the free energy. What are your thoughts about possible ways of including thermal and entropic contributions to your binding energies?

Roy Johnston responded: We haven't included any thermal effects in our calculations yet. I agree that, going forward, it will be important to calculate free energies to enable us to get closer to the experimental studies, which of course are at finite temperatures. The simplest approach would be to include vibrational contributions (at least in the harmonic approximation) to both the energy and the entropy, as these will lead to quantitative changes in the surface binding and adsorption energies, and (probably more importantly) may cause qualitative differences as regards to adsorption site preferences and kinetically preferred reaction pathways.

Stephen Shevlin asked: Is there a significant difference in the binding (*i.e.* atomic charge distribution) of your Janus nanoparticles depending on which face binds to the surface? Would this also have implications for catalytic properties?

Roy Johnston replied: We have calculated the overall metal-to-metal and cluster-to-support charge transfer for the Janus and core shell AuRh clusters (ref. 22 in the paper). For the Au₁₉Rh₁₉ Janus cluster, the Bader charges indicate that a total of 1.31 electrons are transferred from the Rh to the Au half of the cluster. For the Janus-Rh supported cluster (*i.e.* where Rh is in contact with the TiO₂ support), overall 2.50 electrons are transferred to the support, with the resulting total Rh and Au charges being +3.35 and -0.85, respectively. For the Janus-Au supported cluster, only 1.78 electrons are transferred to the support and the Au half of the cluster (which is now in contact with the support) has a small (+0.34) positive charge, with a higher charge (+1.44) on the Rh half. We have not yet analysed the charges on a facet-by-facet basis, but I believe that the surface charge distribution should indeed have an important influence on molecular adsorption and catalytic properties.

Lucas Garcia Verga remarked: I found this paper extremely interesting, especially the analysis about how the support affects different nanoalloys. Your results show that the interactions between metal nanoalloys and the support induce changes in the metal-metal bond lengths for metallic facets close to and far from the support. In the literature, these effects are usually followed by changes in the d-band centres and widths. These are useful electronic descriptors for the binding energies of reactive species such as O and CO in the metallic surface.

I understand that the focus of the work was to assess the stability of the isolated and supported nanoalloys; however, I was wondering if you calculated the shifts of the d-band centres for metallic facets close to and far from the support? If yes, do you see a trend between the shifts of the d-band centres and the binding strengths between nanoalloy and support?

Roy Johnston answered: We have carried out an analysis of the relationships between d-band centres and adsorption energies for CO and O₂ on free 38-atom Au-Rh clusters (ref. 23 in the paper) and for CO on free 38-atom Pd-Ir clusters (ref. 25 in the paper). In all cases, there is no simple correlation due to the importance of elastic (strain) effects in addition to the electronic effects. We have also investigated the relationship between d-band centre and adsorption energy for CO and O₂ on TiO₂-supported 38-atom Au-Rh clusters (ref. 24 in the paper). For the supported clusters, the elastic effects are reduced relative to the free clusters and there is a better correlation between d-band centre and adsorption energy. Going from the free to the supported clusters, there is a downward shift in the d-band centre, which is accompanied by a slight reduction in CO and O₂ adsorption energies. This is consistent with a net transfer of electron density from the nanoalloy to the support (as measured by Bader charges). Finally, I should say that we have calculated overall d-band shifts, not for specific facets, though this would be a good idea for future work.

Caetano Rodrigues Miranda asked: Can you rationalize your findings based on the electronic properties of the systems studied (difference charge densities, bands, size effects, *etc.*)?

Roy Johnston answered: In the Faraday Discussions paper and our other papers cited therein, we have performed analyses based on d-band filling, charge

transfer and elastic (strain) effects and their contribution to the relative stabilities of free and supported pure and bimetallic nanoparticles and to the adsorption energies of small molecules. In some cases, we have found that these effects support each other, but sometimes they act against each other. In particular, surface binding and adsorption energies trends seem to be clearer for Au–Rh than for Pd–Ir.

Nia Richards asked: In your conclusion you use the term “Janus-like structure”. Does this imply that the structures you see are intermediate structures and not fully Janus structures?

Roy Johnston replied: Yes. For example, some of the AuRh nanoparticles are like Janus structures but often with Au overgrowth at the sides of the Rh part (but leaving Rh atoms in contact with the TiO₂ surface), giving rise to “ball-cup” structures, which are intermediate between core–shell and true Janus particles.

Cynthia Friend asked a general question to Rutger van Santen, Roy Johnston and David Willock: In modeling reactions, entropy is important to include. For complex reaction networks, low frequency modes need to be included and we need to go beyond the harmonic approximation. Can you all comment on what advances are needed to accurately include entropy?

David Willock answered: I agree, entropy is an important factor in chemical processes and is largely ignored in most theoretical approaches based on a transition state theory interpretation of potential energy surfaces. As you mention a common way to talk about reaction “Free energy” is to take these minima structures and transition states, perform a frequency calculation and the use the harmonic approximation to extract entropy changes. This is very approximate as low frequency modes have closely spaced energy levels which contribute significantly to the entropy. These are also the modes that have the greatest effect from non-harmonic effects. Entropy due to changes in translational and rotational degrees of freedom are also added in a general way based just on the mass and moments of inertia of the molecules involved in the reaction and the temperature.

What is needed are techniques that sample the immediate region around the key minima and transition states on the potential energy surface so that the number of states that are thermally accessible around each point can be estimated and so the entropy extracted directly. There are many more advanced methods that do this and that have been around for a number of years; Umbrella sampling,¹ transition path sampling,² metadynamics³ among many others. Each of these techniques use some form of molecular dynamics or Monte Carlo simulation to carry out the required sampling. They have been widely applied in biological systems and enzyme catalysis^{4,5} with the use of QM/MM methods to speed up the sampling calculations.

These methods have also been applied to some homogeneous⁶ and heterogeneous catalysis reactions for example in ZnO catalysed methanol synthesis.⁷ These methods do require additional computational time and investment by the researchers to interpret the data in terms of reaction rates. Even so I would expect these methods to become increasingly important in the future.

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- 3 A. Barducci, G. Bussi and M. Parrinello, *Phys. Rev. Lett.*, 2008, **100**, 020603.
- 4 J. L. Gao and D. G. Truhlar, *Annu. Rev. Phys. Chem.*, 2002, **53**, 467–505.
- 5 K. Świderek, I. Tuñón, I. H. Williams and V. Moliner, *J. Am. Chem. Soc.*, 2018, **140**, 4327–4334.
- 6 A. Urakawa, M. Iannuzzi, J. Hutter and A. Baiker, *Chem.–Eur. J.*, 2007, **13**, 6828–6840.
- 7 J. Kiss, J. Frenzel, N. N. Nair, B. Meyer and D. Marx, *J. Chem. Phys.*, 2011, **134**, 064710.

Roy Johnston answered: Manzhos *et al.*¹ have reported the calculation of anharmonic vibrational frequencies and couplings for water on Pt(111) based on DFT calculations and solving the vibrational Schrödinger equation using a neural network. Perhaps such an approach could be used to fit parameters for cubic or quartic vibrational energy functions for cluster-adsorbed molecules.

- 1 S. Manzhos, T. Carrington, K. Yamashita, *Surf. Sci.*, 2011, **605**, 616–622.

Rutger van Santen answered: Since elementary reaction rates depend on activation free energies, it is essential to include properly calculated or estimated activation free energies. Partition functions can be used to calculate those. However the harmonic approximation can only be used for vibrational energies that are large compared to kT . Frustrated rotations are typical examples of modes where non harmonic corrections apply. Especially in zeolite catalysis this is a critical issue, since the intermediate carbenium ions are often nearly free moving. Molecular dynamics-related approaches, quantum-mechanical or quasi-classical have been fruitfully applied. Metadynamics is a quickly developing tool to address this issue.

Richard Catlow remarked: As I commented elsewhere, the landmark paper from Sauer's group¹ calculated entropies and free energies including the contributions of anharmonic terms to the former.

- 1 Piccini *et al.*, *Angew. Chem., Int. Ed.*, 2016, **55**, 5235.

Carlo Lamberti opened discussion of the paper by David Willock: Our experimental evidence on oxides,¹ zeolites² and MOFs³ support your theoretical prediction (DOI: 10.1039/C8FD00005K) that you need to have a reduced Cu(I) site to efficiently bond CO. It will be very interesting if you could extend your theoretical study on the overall redox cycle for CO oxychlorination in order to have a deeper understanding of the structure of the oxychloride phase, the formation of which has been foreseen after interaction of the reduced form of the catalyst with oxygen.^{1,4–8} Finally, as your catalyst contains 10% CuCl₂ and also 8% KCl, if you want to have a realistic picture of its redox property, you should include potassium in your model, because it is known that its presence strongly favors the oxidized state of copper chloride.^{4,6,7}

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- 5 G. Leofanti, A. Marsella, B. Cremaschi, M. Garilli, A. Zecchina, G. Spoto, S. Bordiga, P. Fiscaro, C. Prestipino, F. Villain and C. Lamberti, *J. Catal.*, 2002, **205**, 375–381.
- 6 N. B. Muddada, U. Olsbye, L. Caccialupi, F. Cavani, G. Leofanti, D. Gianolio, S. Bordiga and C. Lamberti, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5605–5618.
- 7 N. B. Muddada, U. Olsbye, G. Leofanti, D. Gianolio, F. Bonino, S. Bordiga, T. Fuglerud, S. Vidotto, A. Marsella and C. Lamberti, *Dalton Trans.*, 2010, **39**, 8437–8449.
- 8 T. Zhang, C. Troll, B. Rieger, J. Kinttrup, O. F.-K. Schlüter and R. Weber, *J. Catal.*, 2010, **270**, 76–85.

David Willock responded: It is good to hear that the experimental evidence from your experimental work also shows this requirement to have Cu(I) present to adsorb CO. We are currently working on models of the chlorination process itself, *i.e.* the transfer of Cl from the lattice to the adsorbed CO. We have also created some higher index planes which require termination with water or OH groups so that the competition between phosgene synthesis and oxidation to CO₂ can be modelled. The introduction of KCl would be a separate study; we have no structural model for the location of the KCl and the way the two chlorides are mixed. This means that constructing a reliable model with KCl present is difficult. A starting point may be to simply dope the CuCl₂ lattice with K⁺ and see the effect on the defect formation energies for the Cl defects that we have presented here.

Paul Sermon remarked: Your paper mentions CuCl₂/alumina ethene oxychlorination catalysts. You characterize your CuCl₂/attapulgite catalyst by CO conversion to Cl₂C=O at 633 K. Your results reminded me of the ethene (1kPa)/He temperature-programmed titration (from 298–773 K at 5 K min⁻¹ (*i.e.* below the melting point of bulk CuCl₂)) of 100 mg CuCl₂/alumina, silica and titania and PdCl₂-CuCl₂/titania catalysts by Keith Rollins.¹ This revealed different peaks (*T*_{max}) of maximum rates of 1,2-ethylene dichloride (EDC) and vinyl chloride (VCM) production, along with integrated numbers of EDC molecules produced overall, that varied with the support and the addition of Pd. Might one be able to titrate your catalysts with CO and see maximum rates of phosgene and CO₂ production (kinetically limited at low temperature and thermodynamically limited above 473 K)? Does the CO₂ come from a shift reaction?

1 K. Rollins and P. A. Sermon, *J. Chem. Soc., Chem. Commun.*, 1986, 1171–1173.

David Willock responded: This is a very good point. In the current paper we have concentrated on the structure of the material used and the removal of Cl from the CuCl₂ lattice during phosgene production. We are also working now on a publication which covers our reactor work in more detail. As you suggest we can titrate the Cl active site with CO monitoring the reduction of phosgene production as a function of time. CO₂ activity follows a similar trend although we have not checked if we can quantify the number of sites involved with CO₂ production and so rule out a water gas shift reaction. Even so the levels of water in the gas feeds are kept as low as possible during these reactions; as we monitor the products

David Willock responded: We have not studied the role of the support and KCl modifier ourselves as we have only presented results for the commercial catalyst. Experiments making a direct comparison of alumina supported CuCl_2 with and without KCl modifiers have been reported.¹ These show that KCl acts to stabilise the higher Cu oxidation state chloride which allows higher temperature operation of the catalysts.

1 C. Lamberti, C. Prestipino, F. Bonino, L. Capello, S. Bordiga, G. Spoto, A. Zecchina, S. D. Moreno, B. Cremaschi, M. Garilli, A. Marsella, D. Carmello, S. Vidotto and G. Leofanti, *Angew. Chem., Int. Ed.*, 2002, **41**, 2341.

Francesca Baletto remarked: In your paper you have shown calculations using two different versions of U, namely 4 and 7, which provide considerably different band gaps of 0.3 and 0.9 eV, respectively. Could you comment on the U effects on surface defect formation, binding energy of CO and charge transfer?

David Willock answered: We have chosen to look at $U = 4$ as a lower limit of the parameter at which a clear band gap appears in the calculation and $U = 7$ which seems to be more widely used in the literature for calculations on Cu salts. The $U = 7$ parameter tends to give defect formation energies around 0.1 eV higher than $U = 4$. However, the trends on comparing the surface defect formation with second layer defects and comparing the small and large supercell results are the same irrespective of the choice of U. So both sets of data show the second layer defect formation energy around 0.1 eV higher than that for the surface layer and the larger supercell giving lower defect formation energies (by up to 0.06 eV). We rationalised this by thinking about the electronic character of the defect. When a Cl^- ion is removed as $1/2 \text{Cl}_2$ the electron remaining will reduce one Cu centre. The U parameter ensures that this electron is localised on one of the Cu centres neighbouring the defect, while a calculation without a U correction would tend to delocalise the electron in the conduction band. It appears that once the U parameter is large enough to introduce a band gap the electron localisation at a Cu centre is ensured and so the results are only relatively weakly affected by the choice of U. For the adsorption of CO the calculated energies also seem to be only weakly affected by the choice of U.

Carlo Lamberti said: I would like to add two comments here. First, in all our studies on the ethylene oxychlorination reaction,^{1–9} we never observed evidence of a measurable fraction of Cu(0) species. Second, there is evidence suggesting that CuCl_2 and $\text{CuCl}_2/\text{CuCl}$ supported catalysts should be in the form of a molten salt under oxychlorination reactions. This holds for both ethylene and CO oxychlorination, that are performed around 200 and 370 °C, respectively. This is obviously very difficult to prove on a structural point of view. Indeed, in our experience the 10 wt% CuCl_2 loaded catalyst on γ -alumina, even at room temperature, exhibits a CuCl_2 phase that is highly dispersed and probably of amorphous nature, as it has been well detected by EXAFS, being however XRD silent. Probably an *in situ* PDF study would be required to fully understand this point.

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- 2 G. Leofanti, M. Padovan, M. Garilli, D. Carmello, A. Zecchina, G. Spoto, S. Bordiga, G. T. Palomino and C. Lamberti, *J. Catal.*, 2000, **189**, 91–104.
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- 4 G. Leofanti, A. Marsella, B. Cremaschi, M. Garilli, A. Zecchina, G. Spoto, S. Bordiga, P. Fiscaro, C. Prestipino, F. Villain and C. Lamberti, *J. Catal.*, 2002, **205**, 375–381.
- 5 C. Lamberti, C. Prestipino, F. Bonino, L. Capello, S. Bordiga, G. Spoto, A. Zecchina, S. D. Moreno, B. Cremaschi, M. Garilli, A. Marsella, D. Carmello, S. Vidotto and G. Leofanti, *Angew. Chem., Int. Ed.*, 2002, **41**, 2341–2344.
- 7 C. Prestipino, S. Bordiga, C. Lamberti, S. Vidotto, M. Garilli, B. Cremaschi, A. Marsella, G. Leofanti, P. Fiscaro, G. Spoto and A. Zecchina, *J. Phys. Chem. B*, 2003, **107**, 5022–5030.
- 8 N. B. Muddada, U. Olsbye, L. Caccialupi, F. Cavani, G. Leofanti, D. Gianolio, S. Bordiga and C. Lamberti, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5605–5618.
- 9 N. B. Muddada, U. Olsbye, G. Leofanti, D. Gianolio, F. Bonino, S. Bordiga, T. Fuglerud, S. Vidotto, A. Marsella and C. Lamberti, *Dalton Trans.*, 2010, **39**, 8437–8449.

Nia Richards asked: Have you investigated the effect of chlorine concentration in the pre-treatment stream, and how does this effect phosgene selectivity?

David Willock replied: In the laboratory experiments for testing phosgene production (see Fig. 1 in the paper), we have tried different concentrations of Cl₂ pre-treatment. The more and the longer Cl₂ is passed, the more phosgene (and less CO₂) is observed. Eventually, the saturation of Cl in the clay was reached and the amount of phosgene produced became constant. In the samples prepared for XANES analysis this saturation level of Cl₂ was used.

Mzamo Shozi asked: Could electron spin resonance be used to detect formation of chlorine radicals during pre-treatment of the catalysts with Cl₂ gas?

David Willock responded: Electron spin resonance would be useful in this area to show how chlorine is stored in the material. We see the formation of CuCl₂ via X-ray diffraction and the XANES data of the chloride catalyst. However, our observations of the oxidation state of Cu as CO flow is introduced may suggest that there are other Cl species on the catalyst and the way that Cl₂ is taken up by this material would be an interesting study in its own right.

Richard Catlow continued the discussion of the paper by Rutger van Santen: How far can we simulate full reaction cycles? There are many examples in the literature and there is no doubt that the field has made great progress in recent years, but can you comment on how reliable the quantitative aspects of the results are?

Rutger van Santen replied: Once the mechanism of the catalytic reaction has been formulated and on this basis elementary reaction rate constants have been computed and the catalytic reaction cycle has been closed, the ordinary differential equations can be formulated that enable us to calculate kinetics of the reaction. There is no automatic procedure to establish the reaction mechanism. One needs to use available experimental or additional computational information to make a proposal and several alternatives have sometimes to be included in the calculations. They may be operated in parallel. It is essential then to, as we do, solve the corresponding microkinetics equations without making an assumption on a rate controlling step. This should come automatically from the simulation.

Implicit to this procedure is the assumption of the mean field approximation. In case reaction intermediates show an inhomogeneous surface distribution, the ODE's may have to be replaced by corresponding Monte Carlo simulations and surface diffusion has to be explicitly taken into account.

When direct comparison is made with experiment, a decision has to be made whether simulations should be done at differential or integral conditions. In the latter case, convection as in reaction engineering simulations has to be at least taken into account. Also, in relation to experiment, one has to be aware that dependent on the evolution of the reaction, the surface state may be close to the initial state, may have converged to a steady state configuration or composition, or is in a state of deactivation. Theory is available that is able to predict the state of a surface in equilibrium with a reactive medium. It may be required to establish this separately from the kinetic simulations because the timescale of surface equilibration or reconstruction may be long compared to that of the catalytic cycle. When simulations are completely "*ab initio*" reliability of the calculations will depend on the accuracy of the used molecular information that is contained in the elementary reaction rate constants.

Generally when DFT simulations are used, activation energies have at least an error of 10 kJ mol⁻¹ and pre-exponents may have substantial errors if only calculated within the harmonic approximation. Care has to be taken that elementary reaction equilibria are correct. Systematic energy errors usually cancel out (except between gas phase and surface), but this will not be the case for reaction entropies. So the use of proper pre-exponents of the elementary reaction rates is essential.

To predict an overall reaction rate properly the temperature of reaction has to be predicted right. This very often depends on the equilibrium of a molecule between the gas phase and the surface. When based on DFT this equilibrium has to be usually adjusted to experiment. In the case of the zeolite simulations we discussed in our paper, the adsorption isotherms of propylene and isobutane based on experimental values took care of this. An additional issue is the question whether the interaction between adsorbates or reaction centers can be considered ideal and lateral interactions can be ignored. In addition to concentration dependent correction terms to reaction energies this may also lead to surface reconstruction effects and island formation. This may be a strong function of conditions.

Clearly absolute catalyst performance prediction by full kinetics simulations have to be considered with care. However, when used to predict trends as a function of surface reactivity, as when Sabatier volcano's are constructed, due to cancellation of systematic errors such simulations may provide considerable insight into the microscopic interactions that determine activity or selectivity differences.

Caetano Rodrigues Miranda asked: How do the variation and errors at DFT level (accuracy and functional dependency) affect and propagate within the microkinetic calculations? Are there studies in this direction on how sensitive or robust the microkinetics model results are regarding the variation of DFT ones?

Rutger van Santen answered: See also my reply to the previous question. The general comment is that for surface reactions that can be considered quasi-equilibrated, systematic errors will largely cancel. This is not the case for

describe catalytic systems in a better way? Which information would you like to obtain from experimentalists in this respect?

Rutger van Santen replied: There is a great variety in DFT computational methods in the way they deal with functionals or basis functions. The advantage of the technique is that many now allow for calculation on complex systems close to those in practice of reaction intermediates as well as transition states in combination with molecular dynamics simulations around local energy minima or maxima. A drawback is the still substantial error in energy accuracy, that is typically still at least 10 kJ mol^{-1} and that it is not trivial to obtain calculated pre-exponents of elementary reaction rates beyond the harmonic approximation. Those are needed for systems with frustrated bending or rotational frequencies or other low frequencies related to the reaction coordinate.

The aim should be to predict properly the spectroscopic properties of adsorption intermediates (less challenging and often doable with spectroscopic accuracy, unless one deals with highly electron correlated systems as the oxides or sulfides. Here there is a need for detailed information of electron structure. High quality first principle calculations embedded in larger matrices are probably the solution) or elementary reaction rates or adsorption energies (for the latter two, experimental numbers of high quality are highly needed).

Richard Catlow opened a general discussion of the papers by Rutger van Santen, Roy Johnston and David Willock: It is important to stress the progress that has been made in the application of modelling techniques in catalytic science. A notable recent development was the landmark paper from Sauer's group¹ which calculated rate constants of catalytic reactions within zeolites with chemical accuracy. These techniques are far from routine, but they illustrate what can now be achieved.

1 Piccini *et al.*, *Angew. Chem., Int. Ed.*, 2016, 55, 5235.

Roy Johnston commented: At present, it is feasible to perform computational studies at a higher level of theory (*e.g.* coupled cluster and Time Dependent DFT) on small clusters in the gas phase, which can be compared with experimental UV-vis and IR spectroscopy (generally involving photodepletion coupled with mass spectrometry), and magnetic or electrostatic deflection measurements. With the development of faster computers and more efficient computer codes (*e.g.* linear scaling DFT), it will be possible to extend these methods to larger clusters and nanoparticles.

Carlo Lamberti asked: Concerning the theoretical work of Sautet *et al.*,¹ predicting the coverage-dependent reshaping of a 13-atoms Pt cluster supported on $\gamma\text{-Al}_2\text{O}_3$ in the presence of different numbers of adsorbed H atoms, it is worth mentioning that at the Operando VI conference Prof. E. Groppo presented work² where she showed synchronous IR (in DRIFT mode), XANES/EXAFS (in transmission mode) and MS data supporting on an experimental ground the theoretical predictions of Prof. Sautet.¹

1 C. Mager-Maury, G. Bonnard, C. Chizallet, P. Sautet and P. Raybaud, *ChemCatChem*, 2011, 3, 200–207.

2 E. Groppo, *Dynamics of reactive species and reactant-induced reconstruction of Pt clusters in Pt/Al₂O₃ catalysts*, presented at Operando VI conference (Estepona, Spain, April 15–19, 2018).

Rutger van Santen replied: This is very nice confirmation of agreement between state of the art computational prediction of the state of small transition metal nanoparticles at ambient conditions and experiment.

Rosa Arrigo commented: With reference to the challenge of electrocatalyst prediction and in particular to the case of the carbon dioxide electrochemical reduction, some of the computational studies present in the literature^{1,2} use the binding energy of for instance carbon monoxide to the surface as a reactivity descriptor. Whilst this static description explains the reactivity towards the formation of C1 products such as carbon monoxide and methane, to explain the formation of C3 molecules using this model one intuitively would invoke a more complex structure of the active sites. To complicate things further, in the case of metals such as Fe³ which is able to dissolve C and form carbides (as opposed to Cu), it could well be that metastable subsurface carbide could be involved in the reaction mechanism. Would it be possible by means of the computational tools available nowadays to model such surface/subsurface dynamics, which are possibly driven by kinetic factors rather than thermodynamics and link this to the products evolved?

- 1 K. P. Kuhl, T. Hatsukade, E. R. Cave, D. N. Abram, J. Kibsgaard and T. F. Jaramillo, *J. Am. Chem. Soc.*, 2014, **136**, 14107–14113.
- 2 A. Bagger, W. Ju, A. S. Varela, P. Strasser and J. Rossmeisl, *ChemPhysChem*, 2017, **18**, 3266–3273.
- 3 R. Arrigo, M. E. Schuster, S. Wrabetz, F. Girgsdies, J.-P. Tessonnier, G. Centi, S. Perathoner, D. S. Su and R. Schloegl, *ChemSusChem*, 2012, **5**, 577–586.

Rutger van Santen responded: For Fischer–Tropsch catalysis there is no correlation between chain growth selectivity and CO adsorption energy. The electrochemically active system that is most selective with respect to hydrogen evolution is the Cu electrode. Also in this case there is no correlation with the CO adsorption strength. The electrocatalytic mechanism that produces longer hydrocarbons is substantially different from that of the Fischer–Tropsch reaction.

As I discuss in the paper, molecular dynamics simulations based on fitted forcefields can be done to study the dynamics and surface reconstruction that result from high adatom coverage and subsurface adatom incorporation.

Graham Hutchings remarked: Returning to the complexity of supported catalysts when made by deposition precipitation it is apparent that atoms, clusters and nanoparticles are all present. The support will have a different influence on each of these as one can envisage a single atom being affected more so than a nanoparticle. Is theory now at a level that it can comment on the reactivity of these different species so we can refine what catalysts we prepare?

David Willock responded: Computer simulation can build models of the structures that we think are important in the catalysis. We have seen in this conference examples of single metal atoms on oxide supports, isolated clusters of metal atoms and discussed the chemical composition of particles in response to

Cynthia Friend asked: There has been a focus on studying materials structure using theory more so than studying reactions in the first session. While this is important, catalysis depends on predicting reactivity and kinetics, meaning that complex reaction schemes and knowledge of elementary steps are required. As noted in my previous question, entropy is also very important. This was demonstrated in Prof. van Santen's paper. He had a network with 140 steps. Confinement in pores of the zeolite was important in the transition state. How can experimental work help constrain this problem so it is tractable? What theoretical advances are necessary to better address these issues?

Rutger van Santen responded: See my reply to your earlier question.

Julien Marbaix opened a general discussion of the paper by Nora de Leeuw: As we know that the cathode in SOFC can be divided into two layers, conduction and reaction, did you try to integrate the incoming oxygen flow to understand its influence on the conductive layer performance?

Nora de Leeuw answered: We did not study the oxygen migration within the YSZ material as we were interested mainly in the geometric and electronic structures of the Ni clusters on top of the oxide. Here, we focused on the behaviour of the metal atoms: whether they prefer to aggregate or wet the surface, their mobility on the surface, and their interaction with the YSZ surface. However, there are other investigations where the authors have performed a theoretical study of the fuel cell, including the migration of oxygen through the electrolyte.^{1,2}

1 X. Wang, K. C. Lau, C. H. Turner and B. I. Dunlap, *J. Power Sources*, 2010, **195**, 4177–4184.
2 S. C. Ammal and A. Heyden, *J. Phys. Chem. Lett.*, 2012, **3**, 2767–2772.

Rutger van Santen commented: Concerning the Monte Carlo simulations of nickel cluster formation, I have a question about whether the elementary rate constants used are reversible. Is there then a relationship between agglomeration time and the overall thermodynamics of the process?

Nora de Leeuw responded: We have performed the kinetics simulation without any restriction in the sense that all the elementary reactions were reversible and individual rate constants were calculated independently for each process. The rate constants are derived from the thermodynamics and they are linked.

Bruce Gates asked: What distances do you find between Ni and O atoms on the zirconia support surface, and what happens if the zirconia is hydroxylated?

Nora de Leeuw responded: The average distance between Ni clusters and the support surface, in Ni_n/ZrO₂(111) and Ni_n/YSZ(111), is 1.9 Å. We have not considered a hydroxylated surface, which might affect the Ni binding to the surface. This could be taken up in a future study, but here we had to start from a simpler case in order to gain initial insight into the Ni clustering on the zirconia and YSZ surfaces.

Parag Shah queried: As the surface is heated up during the simulations, does the Y segregate or move within the surface?

Nora de Leeuw responded: We have not considered segregation effects in the support. We have considered different positions for the Y atoms and noted that, in the most stable configuration, Y is positioned at the top of the surface and as the next nearest neighbour of the oxygen vacancy. We have provided more details about the Y position in YSZ in our previous paper.¹

1 A. Cadi-Essadek, A. Roldan and N. H. de Leeuw, *J. Phys. Chem. C*, 2015, **119**, 6581–6591.

Andrea Russell asked: In your paper you showed that the rate of sintering of the Ni particles was independent of coverage. Do you think that this observation can be accounted for by the fact that you've only considered a high coverage regime and perhaps the rate is only pseudo zero order and may become dependent on coverage at lower overall Ni coverage?

Nora de Leeuw answered: It is correct that we have neglected the lateral interactions of non-bonded Ni, which is a fair approximation as two nickel atoms form a bond from a relatively large distance. We have considered low initial coverage (5%) for Ni₁₀ (Fig. 10(c) in the paper) and found that the sintering rate is similar to an initial coverage of 10% (Fig. 10(d) in the paper). For a low atomic coverage, a single Ni atom might be too far to bind to another structure. We could have included random movements for further evaluation but that was outside the scope of this paper.

Parasuraman Selvam asked: What will happen to the stability and mobility of supported nickel clusters if we start with regular shaped clusters such as tetrahedron (Ni₄), octahedron (Ni₆), icosahedron (Ni₁₂) or cuboctahedron (Ni₁₂) or anticuboctahedron (Ni₁₂) as the starting geometry rather than 1–10 atoms? In fact, in the realistic situation, we get regular shaped clusters/particles, *viz.*, spherical, cubic or isosahedron/cuboctahedron/anticuboctahedron with 2–4 nm sizes onto the supported system. Is it not appropriate to start with such clusters for a rational understanding of the metal–support interaction?

Nora de Leeuw responded: We built our Ni clusters' shape by cutting the Ni(111) surface; a similar approach to previous theoretical studies.¹ Thus, the most stable surface of the cluster is facing the gas phase. We could have also tried other geometries such as tetrahedron (Ni₄) but the result would have been the same, *i.e.* that a 3D shape will be more stable than a flat configuration. This is the main outcome of our study: Ni atoms prefer to aggregate rather than wetting the surface.

1 M. Shishkin and T. Ziegler, *J. Phys. Chem. C*, 2009, **113**(52), 21667–21678.

David Willock remarked: In the transition states you show in Fig. 7 of your paper nickel atoms are moving to join a cluster. It looks like the barrier is to do with diffusion of the Ni atom over the surface rather than a barrier to it joining the cluster. Did you look at different directions of approach for the Ni atom across the

Wilke Dononelli replied: Until now, we have just studied the role of water towards oxygen activation on Au(321) with and without silver impurities and on Au(310).¹ Here, we found that water can be used to activate molecular oxygen in a catalytic cycle with activation barriers of maximum 0.4 eV. Others also found that water might be a possible key in activating oxygen at gold surfaces.² Our calculations indicate that water can enhance the activation of O₂ on gold. On Cu(321) we found an activation barrier of 0.6 eV for the reaction of CO and atomic oxygen. On copper this reaction step seems to be the rate limiting step and not the dissociation of O₂. Here, an associative mechanism might be even more favourable, so the role of water in this context was not determined by our calculations and we cannot give any suggestion about the role of water towards CO oxidation on copper.

1 G. Tomaschun, W. Dononelli, Y. Li, M. Bäumer, T. Klüner and L. V. Moskaleva, *J. Catal.*, 2018, **364**, 216–227.

2 F. Xu, I. Fampiou, C. R. O'Connor, S. Karakalos, F. Hiebel, E. Kaxiras, R. J. Madix and C. M. Friend, *Phys. Chem. Chem. Phys.*, 2018, **20**, 2196–2204.

Francesca Baletto commented: A couple of years ago, we studied the adsorption of CO on various monometallic clusters.¹ We have reported the effect of the addition of Grimme's, DFT-D2 and DFT-D3 corrections, and the optPBE vdW-DF on the site preference of CO. Our study shows clearly the importance of studying the adsorption on the various sites, but it was difficult to say what is the best DFT-functional. It would be quite important to do a close comparison between CCSD(T) and those DFT studies to indicate the best *ab initio* strategy and to quantify clearly the importance of various adsorption sites.

1 J. B. A. Davis *et al.*, *J. Phys. Chem. A*, 2015, **119**, 9703–9709.

Wilke Dononelli answered: In our study we focused on the atop adsorption at the 6-fold low coordinated metal atoms. In your work, you focused on several adsorption positions.¹ The results you present in your work¹ are very interesting. You show that not just quantitative values like adsorption energies but even qualitatively the preferred adsorption site changes depending on the used dispersion correction scheme. As you stated before, it would be highly interesting to make a comparison between your DFT energies and CCSD(T), which we have not focused on, yet. This should be part of a follow-up study.

If other adsorption sites are investigated using the QM/QM' embedding used in our paper, more atoms have to be described in the high level region, as the coordination number of the other surface atoms are higher. This will of course result in higher calculation time. Additionally we will have to check carefully how many atoms have to be considered in the high level region in order to converge the energies of the embedded system to CCSD(T) results.

1 J. B. A. Davis *et al.*, *J. Phys. Chem. A*, 2015, **119**, 9703–9709.

Francesca Baletto remarked: What are the differences in the adsorption energy for various adsorption sites?

Wilke Dononelli replied: On a M₅₅ nanoparticle two different atop positions and additional positions between two and three metal atoms may be possible

With a formal scaling of N^7 the calculation time would be 2^7 times as long. Even if one naively suggests that an inversion centre or mirror axis would enhance the speed of the calculation by a factor of two, then no speed-up can be achieved by doubling the size of the subsystem. For these systems with 55 metal atoms in our embedding scheme, adding another adsorbate would always result in much higher calculation times.

David Willock commented: In your CCSD(T) calculations the effect of dispersion interactions between the adsorbate and the metal cluster will be taken into account. In the DFT calculations it is now common practice to introduce dispersion using an additional parameterised term (*e.g.* D2 or D3 corrections). Can you make a comparison of your DFT and CCSD(T) results to make some comment on the accuracy and appropriateness of such dispersion corrections? This seems particularly important for metal nanoparticles for which an atom-by-atom parameterised calculation of dispersion seems difficult to justify.

Wilke Dononelli answered: Thank you for this question. There is an ongoing debate about using semi-empirical corrections like D2 or D3, where in most cases people use additional DFT functionals in order to give a statement about whether dispersion corrections have to be used or not. We calculated the adsorption energy of CO on Au₁₃ using D3. Without dispersion correction we found $E_{\text{ads}} = -1.21$ eV at the PBE level of theory. Using D3 we found -1.30 eV. At the CCSD(T) level of theory we found -0.88 eV as shown in our paper. On Au₅₅ we found $E_{\text{ads}} = -0.84$ eV for PBE, $E_{\text{ads}} = -0.86$ eV for CCSD(T)/PBE and $E_{\text{ads}} = -1.00$ for PBE-D3. If we claim that CCSD(T) gives good results, then PBE-D3 seems to overestimate the binding strength of CO. An indication for difficulties in the parametrisation you are mentioning may be seen in the differences of the total energies. The total energy of CO in the gas phase using pure PBE or PBE-D3 is virtually identical, whereas the absolute value of the total energy of Au₅₅ is 17.53 eV ($\sim 11\%$) higher for PBE-D3 compared with pure PBE. This should not be a statement that dispersion corrections are incorrect in a general sense. For example, others showed that in the case of alcohols or alkoxy species, van der Waals interactions might be favourably described by using semi-empirical dispersion corrections.¹

1 Y. Xu, W. Chen, E. Kaxiras, C. M. Friend and R. J. Madix, *J. Phys. Chem. B*, 2018, **122**, 555–560.

Alexander Genest remarked: The results of your plane-wave based methods and your atom-centered basis set methods matched perfectly, even though they should not due to the basis set superposition error (BSSE), which affects only the latter approach. Did you correct the results of your atom-centered results for this error? Do you have an estimate for the magnitude of the error?

Wilke Dononelli responded: In our atom-centred based calculations we did not consider the BSSE. As a first step we tried to find a basis set where we find adsorption energies at the PBE level of theory that were in good agreement with calculations using the PAW method. The adsorption energies calculated using the two different methods only show the same results by chance. Using the counterpoise correction (CP correction) by Boys and Bernadi, we find an adsorption

Table 1 Excitation energies of M_{13} and M_{55} nanoparticles ($M = \text{Au}, \text{Ag}$ or Cu). Energies in eV

Nanoparticle	E^* in eV
Au_{13} (EOM-CCSD)	0.29
Au_{13} (TD-PBE)	0.20
Au_{55} (TD-PBE)	0.07
Ag_{13} (EOM-CCSD)	0.20
Ag_{13} (TD-PBE)	0.15
Ag_{55} (TD-PBE)	0.07
Cu_{13} (EOM-CCSD)	0.12
Cu_{13} (TD-PBE)	0.13
Cu_{55} (TD-PBE)	0.07

In the second part of your question you are giving good insight into the understanding of the influence of d-orbitals or d-bands to chemical bonding in metal-adsorbate interactions. In our study, we compared VASP calculations using the PAW approach to Gaussian calculations where we used a Hay and Wadt basis set with pseudo potentials. The basis set was chosen in order to give good results with respect to the adsorption energies calculated with VASP at the PBE level of theory. Within these two different approaches, two different ways of including the d-valence electrons were used. Both methods result in similar adsorption energies of CO on the same nanoparticle (using PBE). Relativistic effects have been taken into account by using pseudo potentials. We think that your comment about the repulsive character of doubly occupied d-orbitals of the metal nanoparticles could be correct. In order to investigate the role of electron correlation, a possible way could be to freeze the electrons of the MOs constructed from the d-AOs during the correlation part of the calculation. The resulting adsorption strength should be stronger. The difficulty will be to decide which molecular orbitals have to be considered. Your argument is based on a one-particle picture, which might be difficult to transfer into a many particle perspective. In addition, binding should be a local phenomenon, whereas orbitals in metal nanoparticles exhibit a delocalised character. Despite these difficulties, we will try to examine your comment in future work.

To answer your last question, we summarised the wavenumbers of CO stretching vibrations in the gas phase and on the different Au nanoparticles calculated at the PBE level of theory in Table 2. Comparable to metal carbonyl species a red shift of the CO stretching frequency (compared to CO in the gas phase) was observed for all systems in our investigations. However, due to the different nature of the electronic structure of different sized nanoparticles no simple correlation between the bond strength and the shift in frequency can be made.

Valerii Bukhtiyarov asked: When you study oxygen adsorption on Group 11 metals, you try to compare the activation energy of adsorption on different clusters. Are there any differences in oxygen adsorption on Ag_{13} and Ag_{55} clusters? I mean the activation energy of adsorption or subsequent reactivity of adsorbed oxygen species.

Table 2 CO stretching frequencies on different Au surfaces and nanoparticles calculated at the PBE level of theory. Wavenumbers are given in cm^{-1}

Surface/nanoparticle	Wavenumber in cm^{-1}
CO-Au(321)	2056.9
CO-Au ₅₅	2058.5
CO-Au ₁₃	2076.7
CO _{gas}	2122.8

Wilke Dononelli answered: In the underlying study, we compared the dissociation energy of O₂ on M₅₅ (M = Au, Ag or Cu) nanoparticles to dissociation barriers on periodic M(321) surfaces. Additionally, we focused on the adsorption energy of CO on M₁₃, M₅₅ and M(321). We did not focus on reaction barriers of oxygen and other molecules on M₁₃ nanoparticles or adsorption energies of oxygen on M₁₃ or M₅₅ nanoparticles. Nevertheless, we can use the geometries of the initial state of the O₂ dissociation reaction on the M₅₅ nanoparticles and the M(321) surfaces to calculate the adsorption energies of these geometries as shown in our paper. Here, E_{ads} is calculated as:

$$E_{\text{ads}} = E(\text{O}_2, \text{adsorbed}) - E(\text{O}_2, \text{gas phase}) - E(\text{surface})$$

The adsorption energies are listed in Table 3.

Bruce Gates opened discussion of the paper by Arunabhiram Chutia: What happens when the isolated positively charged/negatively charged gold species on the support surface are probed with CO?

Arunabhiram Chutia replied: Based on whether the CO probe molecule is adsorbed on the isolated positively or negatively charged Au species it may display different electronic properties, *i.e.*, if CO is adsorbed on a negatively charged Au species then the antibonding π^* orbitals of CO will be populated weakening the C=O bonding. On the other hand, if CO is adsorbed on a positively charged species it may give an opposite effect. Therefore, a calculation of vibrational frequency for CO adsorbed on negatively charged Au may give a lower frequency compared with CO adsorbed on a positively charged Au species. This is certainly something we will be considering as we extend our work further.

Carlo Lamberti commented: I found very interesting the in-depth knowledge of the electronic density of states (DOS), both occupied and non-occupied, of the

Table 3 PBE adsorption energies for O₂ on M₅₅ and M(321) surfaces (M = Au, Ag or Cu). Energies are given in eV

Surface/nanoparticle	E_{ads} in eV
Au(321)	-0.15
Au ₅₅	-0.25
Ag(321)	-0.43
Ag ₅₅	-0.42
Cu(321)	-1.24
Cu ₅₅	-1.56

Francesca Baletto asked: In the near future of first-principle calculations applied to investigate metallic nanoparticle properties, what is your suggestion about the use of DFT+U in comparison with other schemes, such as CCSD(T), TD-DFT and GW?

Arunabhiram Chutia responded: The DFT+U methodology takes into account strong on-site Coulomb interaction of localised electrons and has been widely used to explore the electronic structure of materials with f-electrons and metal oxides. A recent study by Beridze *et al.* suggested that use of DFT+U, with the Hubbard U parameter derived by *ab initio* methods could be a good choice over CCSD(T); the reason being that even though the CCSD(T) method gives a very accurate electron correlation energy, this method is however computationally very expensive and can be used to study small clusters.¹ However, as we heard from our previous speaker (Dononelli *et al.*), with a combination of CCSD(T) and DFT methods employing the QM/QM scheme, we can perform more accurate calculations and in the near future this could be perhaps routinely done. On the other hand, if we are interested in studying the excited states of these materials then we can employ the TDDFT+U method. In this regard it is also worth mentioning that recently, Tancogne-Dejean *et al.* reported the implementation of self-consistent DFT+U and TDDFT+U methods.² So far as the GW method is concerned, similar to other Green's function approaches, it replaces the unknown XC-potential by a self-energy and in recent years it has been able to calculate transport properties of single molecules, and correctly predicted the band gap of a large number of semiconductors. In terms of the computational cost, it is also expensive, however, in due course we may be able to use this method more routinely. Finally, the choice of methods greatly depend on which properties of materials we are looking at.

1 G. Beridze *et al.*, *J. Phys. Chem. A*, 2014, **118**, 11797–11810.

2 N. Tancogne-Dejean *et al.*, *Phys Rev. B*, 2017, **96**, 245133.

Nora de Leeuw responded: DFT+U and GW are usually used to improve the calculated band gap of semiconductors and insulators, in comparison with the experimental results. CCSD(T) and TD-DFT are employed to study excited states. Neither of those properties are in the scope of our paper as we are interested in the electronic and geometric structures, and the mobility of the Ni clusters on the oxide surfaces. Additionally, the next step is to study the reverse water gas shift reaction at the interface between the cluster and the oxide surfaces: this does not require any of the latter techniques that are more time consuming than DFT.

Cynthia Friend commented: In order to evaluate whether water produced *in situ* can promote O₂ dissociation, the short lifetimes of both O₂ and water need to be considered. Dioxygen specifically is very weakly bound and will have a short surface lifetime under reaction conditions. Kinetic modeling that accounts for such a short lifetime under specific conditions needs to be considered.

Wilke Dononelli replied: You are completely right. Especially the adsorption strength of O₂ is very weak. By co-adsorption of water and O₂ the adsorption

