

## Catalyst design from theory to practice: general discussion

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**Hans-Joachim Freund** opened the discussion of the paper by Alberto Roldan: How is the atomic hydrogen produced on the greigite surface? In the paper (DOI: 10.1039/C5FD00186B) there is no comment whether you studied dissociate hydrogen adsorption.

**Alberto Roldan** answered: We agree with Prof. Freund that we have not studied the hydrogen dissociation on the surface. However, the experiments are carried out on small nanoparticles exposing different surfaces and edges where H<sub>2</sub> molecules dissociate, as DRIFTS tests (not published) have suggested by the formation of reduced carbonated species.

**Rutger van Santen** remarked: According to Wachterhauser, the reactive phase is Mackinawite. This is a layered FeS phase. The S may also have a higher reactivity than that of Greigite. How does the activation of H<sub>2</sub> on Greigite compare with that of Mackinawite, and would the reactivity of S be such that SO groups form in the surface that helps to generate CO? The SO group can have a subsequent reaction with H<sub>2</sub>S to give S<sub>2</sub>, which would help to transform the Mackinawite to pyrite.

**Alberto Roldan** replied: Although the reactivity of Mackinawite is not within the scope of this paper (DOI: 10.1039/C5FD00186B), we know that CO<sub>2</sub> adsorbs stronger on its surfaces than on greigite<sup>1</sup> and therefore it is worth considering FeS as a catalyst. We are currently also investigating the reactivity of Mackinawite but a detailed comparative study is still missing.

1 N. Y. Dzade, A. Roldan and N. H. de Leeuw, *J. Chem. Phys.*, 2015, **143**, 094703.

**Michail Stamatakis** said: Including the zero point energy (ZPE) corrections for the initial, transition and final states of the reactions will shift these energies to higher values. Are these shifts uniform among these different states, or do you see significant differences in the ZPE of the reactants *versus* the products, for instance? Since hydrogenation steps involve (presumably mobile) H adatoms being incorporated into the C1 fragments, it is conceivable that the vibrational frequencies change significantly, thereby resulting in non-uniform shifts.

**Alberto Roldan** responded: The energy contribution of the ZPE to the total energy slightly shifts the profile and only the activation energies would change (but by less than 0.1 eV). Thus, the general trend and viability of the process is not compromised.

**David Willock** continued: You show that there are two iron species on the surface, Fe(A) and Fe(B), and it appears that Fe(B) responds much more strongly to adsorbates. Is this due to the co-ordination of these cations on the surface? Did you consider competitive adsorption of other molecules (especially water) at these sites that may change the effective calculated adsorption energies?

**Alberto Roldan** replied: That is right, both FeA and FeB at the surface are under coordinated, especially FeB which occupies an octahedral site but it is only 3-coordinated. Both sites FeA and FeB respond to the presence of molecules leading to competitive adsorptions, *e.g.* carbonate and H<sub>2</sub>O.<sup>1</sup>

1 A. Roldan, N. Hollingsworth, A. Roffey, H.-U. Islam, J. B. M. Goodall, C. R. A. Catlow, J. A. Darr, W. Bras, G. Sankar, K. B. Holt, G. Hogartha and N. H. de Leeuw, *Chem. Commun.*, 2015, **51**, 7501.

**Albert Bruix** asked: The *U*-correction provides a computationally feasible improvement to the poor description of systems with strongly correlated electrons by standard LDA and GGA exchange–correlation functionals. However, some calculated properties, including adsorption energies, have been found to depend on the choice of the *U* parameter. The effect on calculated adsorption and reaction energies is particularly significant when these processes involve changes in the occupation of the d and f orbitals in transition and rare-earth oxides, respectively. Could you comment on how the choice of *U* may affect the calculated mechanisms? Are there any steps, such as hydrogen adsorption, which involve charge transfer to or from the Fe 3d orbitals?

**Alberto Roldan** answered: We followed the Hubbard approach to accurately compute the d-Fe electron correlation. Although small ( $U_{\text{eff}} = 1$  eV), this approach provides a better description of the electronic structure (DOS) of the material and therefore its redox properties. However, the Fe surface is not the species responsible for the transfer of electrons to CO<sub>2</sub> of the H-adatoms, the nearby S is the electron transfer site, as explained in the manuscript.

**Wataru Ueda** remarked: Heterogeneous catalysis researchers often try to mimic bio-enzymatic systems with solid-state materials with the same elemental constituents. However, catalytically active sites in the enzymatic systems always

assume discrete structures. On the other hand, simple solid-state materials contain repeated structures of discrete sites. Therefore, solid-state materials cannot mimic enzymatic systems, unless solids are constructed with structurally isolated discrete units. Thus, we need new design concepts and a new methodology of materials synthesis. What do you think about this?

**Alberto Roldan** replied: I do agree that enzymes and extended materials cannot be directly compared, not only because enzymatic catalytic centres are discrete structures but also because they have the backbone around these structures to stabilise the sites and the reaction intermediates. Nevertheless, enzymes can provide useful hints to explain the behaviour of extended materials. Particularly in our case, we followed the suggestions in Origin of Life theories, which hypothesized that extended [Fe-S] structures could have been predecessors of contemporary enzymes.

**Elad Gross** commented: Can you identify any similarities between the heterogeneous and enzymatic catalysts as you decrease the size of  $\text{Fe}_3\text{S}_4$ , making it comparable to the core size of the enzymatic catalyst?

**Alberto Roldan** replied: The enzymatic cluster is surrounded by a backbone that may stabilise intermediates in the reduction process. This is lacking on the pristine surface and therefore the mechanism is not necessarily the same. It has been shown, for instance, that small clusters of  $\text{Fe}_4\text{S}_4$  are not stable once they are exposed to reactants. Another example are the chalcogels,<sup>1</sup> whose poor electronic conductivity reduces their activity towards reductive processes. Thus, although the active centre is very similar, the backbone surrounding them makes enzymes able to catalyse the reduction in very specific conditions.

1 B. D. Yuhas, C. Prasittichai, J. T. Hupp and M. G. Kanatzidis, *J. Am. Chem. Soc.*, 2011, **133**, 15854.

**Joachim Sauer** opened the discussion of the paper by Dimitrios Manganas: I understand that from including the spectra of all models and fitting to the observed spectra you reach the conclusion that different sites are present and that dimeric structures are dominating. The fit will of course get better with an increasing number of structures included in the fit.

What did you do to make sure that the structures you include are significant in the statistical sense?

**Dimitrios Manganas** replied: All calculated spectra were normalized and constant energy shifts and broadening Gaussian parameters were applied as described in the text. Comparison with the experimental spectra was performed via a least squares fitting procedure as described in the supporting information, using  $R^2$  as a measure of the goodness of fit. In fact, it was found that this process is satisfactorily sensitive with respect to the degree of oligomerization and the number of structures included in the statistical analysis. For example, as it is discussed in the section 'X-ray spectroscopy', the individual V L-edge spectra of the A and B-domain type structures containing V–O–V bridges ( $\text{V}_2\text{Si}_6\text{H}_6\text{O}_{14}$ ,  $\text{V}_2\text{Si}_{12}\text{H}_{12}\text{O}_{23}$ ,  $\text{V}_3\text{Si}_5\text{H}_5\text{O}_{15}$  and  $\text{V}_4\text{Si}_4\text{H}_4\text{O}_{16}$ ), provide the best agreement between

theory and experiment, in terms of relative intensities and intensity distribution, especially for the  $L_3$  resonances located at 516, 517.5 and 519 eV. Moreover, by averaging over the above four structures (Fig. S8 DOI: 10.1039/C5FD00193E), the average spectrum has a closer resemblance with the  $V_2O_5$  spectrum. There are of course limitations. Although comparison of individual spectra can be conclusive for specific coordinating groups (e.g. umbrella type monomers), it cannot clearly distinguish between monomers and oligomers. The situation is improved when a simultaneous comparison between the three experiments is performed.

Once again, it should be highlighted that this procedure describes a molecular protocol that is developed to provide spectra-structure correlations. Hence, in this present form it cannot provide safe interpretations for a particular catalytic center unless spectra under *in operando* conditions are provided and reaction intermediates through accurate energetic studies are identified.

**David Willock** continued: How well are the calculations and spectroscopic measurements able to distinguish between the trimer structures and larger oligomers of  $VO_x$  species?

**Dimitrios Manganas** responded: A quantitative estimation regarding the degree of oligomerization is a rather challenging task that would require much more experimental information for conclusive interpretations. Nevertheless, it was observed that trimeric structures in 'closed form' are not only able to reproduce three individual spectroscopic experiments (Raman, V L-edge and O K-edge), but they also provide very good agreement for the relative intensities of the V L-edge and O K-edge spectra. Moreover, by averaging over the monomers, dimers, trimers and tetramers, the resulting V L-edge spectrum has a close resemblance with the  $V_2O_5$  spectrum, rather than with the V loading spectra shown in Fig. S8 (DOI: 10.1039/C5FD00193E). Based on these observations, it seems that the presented combined experimental and theoretical protocol is sensitive with respect to the degree of oligomerization at least to some extent.

**Bert Weckhuysen** remarked: I appreciate the combination of different experimental methods, as well as their theoretical validation in order to shed new insights in the field of supported vanadium oxide catalysis. The novel aspect is certainly related to the interpretation of the L-edge vanadium X-ray absorption spectroscopy, as well as in the combination of the different methods, culminating in Fig. 13 of DOI: 10.1039/C5FD00193E. I have, however, a few questions.

1) Did you try to use another support oxide to test your hypothesis? In other words, what would be the effect of (additional) hydroxyl groups in the way the species are attached to the surface, and what would it mean for the relative ratio of isolated *vs.* oligomeric vanadium oxide species, differing in their number of vanadium oxide species.

2) Did you try to use oxygen-18 and how this would influence the Raman spectra, as well as the other spectra? It would be interesting to notice then what the relative changes are in the different spectra. One would also be able to calculate such spectral changes. It would be another way to validate the conclusion you have made.

3) Fig. 12 (DOI: 10.1039/C5FD00193E) is very absolute in terms of what the relative amount is of specific oligomeric vanadium oxide species. How sure are we

that this is indeed the situation? What would happen when *e.g.* water is added to the system?

**Dimitrios Manganas** replied: As is stated above, multiwavelength Raman studies have been used to identify species on silica supported vanadia oxide catalysts including analysis of overtones,  $^{18}\text{O}$  labeling and discussing the resonance enhancement mechanism of particular signals (ref. 25 DOI: 10.1039/C5FD00193E). However, even such integrated Raman analysis cannot be conclusive about the catalytic active sites, leaving this concept an open discussion field (ref. 26 DOI: 10.1039/C5FD00193E). This is exactly why multimethod experimental and theoretical spectroscopic protocols with even higher predictive power need to be developed.

The current work (DOI: 10.1039/C5FD00193E) provides a first step towards this direction. We are in the process of extending the available experimental data towards spectroscopic investigations that are more related to the actual structural conditions of the catalytic centers. Moreover, we are planning to transfer this problem in the field of reactivity and study the energetics of the catalytic systems on particular reactions. It will be only then, when structural combinations as those presented in Fig. 12 (DOI: 10.1039/C5FD00193E) may be thought to be relevant to the active catalytic center. For the time being they just provide confident structure-spectra correlations.

**Bruce Gates** asked: You referred to 'spectroscopic response to structural correlation'. Could you please explain what this means?

**Dimitrios Manganas** answered: In this work (DOI: 10.1039/C5FD00193E), by choosing a vanadium molecular catalyst of well-defined geometry and oxidation state and by calculating its main spectroscopic properties in terms of rRaman and X-ray absorption, we could define an analysis protocol that relates structural information to electronic structure information to spectroscopic properties. The same protocol could be applied to identify the structure and composition of the molecular species that dominate the spectroscopic properties of a silica-supported vanadia catalyst. Of course, such observation cannot be translated to direct information about the active catalytic species, as this requires further studies by transferring the problem in the field of reactivity. This is, however, one more example that demonstrates that molecular protocols, which are widely used in field of homogenous catalysis, are also applicable to a large extent in the more challenging field of heterogeneous catalysis.

**David Willock** enquired: The Raman modes responsible for spectral lines are often thought of as quite localised effects, bond stretching, bending, *etc.* How much information on extended structure are you likely to be able to obtain?

**Dimitrios Manganas** answered: It is perhaps safe to say that actually the majority of the spectroscopic techniques can be considered to a large degree local in nature, probing the local structure of a studied system. Interestingly, in the case of  $\text{V}_2\text{O}_5$ , the shape of the V L-edge XAS spectrum has been proven sensitive to the bulk structure of the solid, but not the corresponding O K-edge one (ref. 33 and 35 DOI: 10.1039/C5FD00193E). Hence, it seems that the investigation of the

effects due to the extended structure would require further information by addressing such questions, *e.g.* in the field of reactivity.

**Joachim Sauer** continued: I do not think that you have made sufficiently clear what is new in your approach compared to well-established concepts in surface science and heterogeneous catalysis. The comparison of surface structures with inorganic model compounds (the similarities and differences) has a long history. I mention only the early work of Muetterties on metal carbonyls<sup>1</sup> and a 1989 Chemical Reviews article with the title 'Molecular Models in ab Initio Studies of Solids and Surfaces'.<sup>2</sup> As far as a local probe is concerned, the spectroscopic techniques may differ in the locality for an individual site, but there may be site-site interactions, and after all you observe a signal that is an average for the sample you are looking at.

1 E. L. Muetterties, *Science*, 1977, **196**, 839.

2 J. Sauer, *Chem. Rev.*, 1989, **89**, 199.

**Dimitrios Manganas** answered: Indeed combining theoretical and experimental multimethod protocols is a practice with long history that has been successfully applied in the fields of homogeneous and heterogeneous catalysis. In general, the more spectroscopic information using various spectroscopic techniques is available, the more reliable the derived structure/activity relationships will be. In this work (DOI: 10.1039/C5FD00193E) apart from rRaman and O K-edge spectroscopies that have been successfully used in the past for structure to spectra correlations, V L-edge spectroscopy is introduced in addition.

It must be highlighted that interpretation of metal L-edge spectra is a challenging task as the open core p-shell is subject to strong spin orbit coupling (SOC), which splits the spectrum into L<sub>3</sub> and L<sub>2</sub> edges and strongly mixes the 'non-relativistic' final states. In that respect, it is only possible to achieve first principles quantitative description of the experimental spectra by a) constructing all possible electron configurations involved in the L-edge excitation process, b) accounting for electron dynamic correlation and c) properly describing the spin-orbit coupling and covalent interactions. In addition, since metal L-edge spectroscopy is widely applied in the field of solid-state chemistry and heterogeneous catalysis, a successful methodology should also be able to operate on sufficiently large cluster models and in a predictive fashion. This has all been taken into account in the DFT/ROCIS method development.<sup>1-3</sup>

In this concept, this work (DOI: 10.1039/C5FD00193E) presents a computational protocol based on advanced theoretical spectroscopy combining rRaman, O K-edge and V L-edge X-ray spectroscopies, that are used to establish structure-spectra relationships in the field of vanadia catalysts. In a more general spirit, the need of a simultaneous interpretation of the available spectroscopic data of the studied systems is emphasized.

1 M. Roemelt and F. Neese, *J. Phys. Chem. A*, 2013, **117**, 3069.

2 D. Maganas, S. DeBeer and F. Neese, *Inorg. Chem.*, 2014, **53**, 6374.

3 M. Roemelt, D. Maganas, S. DeBeer and F. Neese, *J. Chem. Phys.*, 2013, **138**, 204101.

**Bert Weckhuysen** said: What would happen if you use another Raman laser excitation frequency? I notice that you have a 450 nm band as the sample seems to

have a light orange colour. This absorption band is considered to originate from oligomeric species. What would happen if you excite with another Raman laser source? What would be the effect of the (dominant) molecular structure of the supported vanadium oxide species you have proposed.

**Dimitrios Manganas** answered: This is a very valid question that needs to be explored. We are currently in the process analyzing multiwavelength rRaman spectra of the system.

**Annette Trunschke** remarked: An additional comment from the experimentalists regarding ongoing experimental work: currently we are studying vanadium oxide species with variable degrees of oligomerisation at the surface of different supports by application of a set of complementary spectroscopic techniques, including UV-vis, X-ray absorption, and Raman spectroscopy. The Raman spectra are measured by applying different excitation energies in the range between 325 and 633 nm.

**Bert Weckhuysen** replied: This is indeed a very good strategy to give further understanding to this important catalyst system, *i.e.* multiple characterization techniques, including Raman spectroscopy with different excitation energies, as applied on supported vanadium oxide catalysts varying in their V oxide loading (and therefore most probably a different degree of oligomerization/polymerization).

**Bert Weckhuysen** continued: What would happen if you used molybdate instead of tungstate? How unique is this catalytic behavior in relation to the tungstate in your material?

**Annette Trunschke** answered: Tungstates and molybdates have been studied before in alkane oxidation, but usually reaction temperatures above 500 °C have been applied to achieve appreciable conversion. Hydrothermally prepared MnMoO<sub>4</sub> composed of large primary particles (not nano-structured) showed selectivity to propene between 60 and 80% (depending on the preparation technique) in the oxidative dehydrogenation of propane at conversions between 3 and 10%. However, a reaction temperature of 500 °C was necessary to achieve these conversions due to the low specific surface area of the materials (1–7 m<sup>2</sup> g<sup>-1</sup>). Consequently, high selectivity can also be achieved over manganese molybdate at conversions comparable to those adjusted for manganese tungstate. The unique feature of the presented MnWO<sub>4</sub> catalyst is its high activity and selectivity at temperatures as low as usually applied for vanadium oxide catalysts. Efforts in the synthesis may lead to optimized properties of MnMoO<sub>4</sub> catalysts as well.

**Joachim Sauer** remarked: The use of a different excitation wavelength in Raman spectra proved crucial in an early study of VO<sub>x</sub>/SiO<sub>2</sub> and VO<sub>x</sub>/Al<sub>2</sub>O<sub>3</sub> systems.<sup>1</sup>

1 N. Magg, B. Immaraporn, J. B. Giorgi, T. Schroeder, M. Bäumer, J. Döbler, Z. Wu, E. Kondratenko, M. Cherian, M. Baerns, P. C. Stair, J. Sauer, H.-J. Freund, *J. Catal.*, 2004, **226**, 88.

**Dimitrios Manganas** responded: I fully agree that studies like the one by Magg *et al.* have been proven instrumental in establishing structure-spectra correlations in the field of the vanadia oxide catalysts.

**Andrzej Kotarba** asked: Different excitation energies will lead to laser beam penetration of an investigated material to a different extent, so the Raman spectrum would change accordingly. Do you include this effect in your modelling when constructing the structure-spectra relationship?

**Dimitrios Manganas** answered: Indeed multiwavelength Raman studies have been used to identify active species on silica supported vanadia oxide catalysts (see for example ref. 26 DOI: 10.1039/C5FD00193E. We are in the process of revisiting such experiments and extending the analysis towards this direction.

**Bruce Gates** opened the discussion of the paper by Craig Plaisance: Could you make a precise statement of what your catalyst design principles are?

**Craig Plaisance** replied: We want to design an active site in which the two oxidation steps ( $H^+ + e^-$  removal) preceding water addition have associated oxidation potentials equal to the operating potential of the anode. These two steps effectively 'prime' the catalyst to carry out water addition by storing the energy supplied by the external potential in the form of holes localized on the active site. The more endothermic these two steps are, the more energy is stored in the holes, leading to more exothermic water addition. If these two steps have oxidation potentials equal to the operating potential of the anode, then we are effectively storing in the active site 100% of the energy supplied by the external potential in order to drive the water addition step.

**David Willock** said: The quasiatomic orbitals look like a very useful tool to extract chemically intuitive information from periodic DFT. But, could you explain how the quasiatomic orbitals exactly reproduce all of the ground state properties? Surely the plane wave basis can be extended indefinitely and so must be more complete than the minimal basis used for the quasiatomic orbitals.

**Craig Plaisance** answered: The key point is that they exactly reproduce the ground state properties, *i.e.* the occupied orbitals, not the entire band structure. As long as there are more quasiatomic orbitals (QOs) than there are electrons, one can describe all of the occupied states within the subspace spanned by the QOs.

**Ludovic Briquet** asked: How accurate is your method to compute energy barriers? And how does it compare to other methods such as Nudged Elastic Bands?

Could your model be used to screen the activity of several different materials in a reasonable time frame? The kinetic treatment requires evaluation of the energy barriers, which could be computationally intensive.

**Craig Plaisance** answered: The method we use is accurate as long as the reorganization energy of the modes normal to the reaction coordinate between the two potential energy surfaces is not significant. We have not tested this



assumption, but it is something we are planning to look at in the future. It would actually not be difficult to include this reorganization energy using Marcus theory at a fixed point along the reaction coordinate and we will likely do this in future studies. NEB calculations are not applicable for calculating these barriers since the transition state is not a saddle point on a single potential energy surface.

The calculation of barriers is much more expensive than calculating only the reaction energies. It is possible, as we show in the paper (DOI: 10.1039/C5FD00213C), to determine a linear free energy relationship between the barrier and the reaction energy that could be used in the screening studies. The design principle we present in the paper (DOI: 10.1039/C5FD00213C) requires only reaction free energies, although it is derived from kinetic treatment.

**Andrzej Kotarba** said: The cobalt spinel is a very good catalyst for  $\text{N}_2\text{O}$  decomposition. We have investigated the system and optimized it by doping and engineering the nanocrystallite morphology for several years. In the  $\text{deN}_2\text{O}$  process, after reactive  $\text{N}_2\text{O}$  adsorption resulting in  $\text{N}_2$  release, the recombination of surface oxygen is the rate limiting step. In real conditions, the catalyst works in the presence of water vapour. So, similarly to your process, the affinity to oxygen and water is a key factor for the cobalt spinel's catalytic performance. Obviously, they are different at various facets. For  $\text{deN}_2\text{O}$  we have found  $\text{Co}_3\text{O}_4$  (100) as the optimal one. The DFT calculated surface energies of the facets increased in the following order:  $1.39 \text{ J m}^{-2}$  (100) <  $1.48 \text{ J m}^{-2}$  (111) <  $1.65 \text{ J m}^{-2}$  (110). At the same time these facets are most often observed experimentally for  $\text{Co}_3\text{O}_4$  nanocrystals.<sup>1</sup> Was there a particular reason for the selection of (110) and (311) surface? One of the conclusions in the paper (DOI: 10.1039/C5FD00213C) is that the system is sub-optimal. What do you have in mind? Does the molecular modelling give us any hints or guidance for the optimization of the catalyst's performance *e.g.* by bulk or surface doping?

1 F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. J. Kurzydowski and Z. Sojka, *J. Phys. Chem. C*, 2011, **115**, 6423.

**Craig Plaisance** responded: The (110)-B surface was chosen because it does not contain pairs of adjacent Co cations in the surface like the other terminations, but only isolated Co cations. Such a site corresponds to the 'slow' site proposed by Frei and coworkers,<sup>1</sup> while the 'fast' site they propose consists of the pair of coupled Co cations. One goal of our work (DOI: 10.1039/C5FD00213C) was to examine whether such a dual-Co site was in fact more active, so it was important to also examine a single-Co site.

The (110)-A surface was chosen because it is the only termination on which a  $\mu^2$ -oxo species can be formed.

The reason for choosing the (311) surface is rather complex and it took us some time to come up with it. The problem with the (001) surface is that one of the protons in the active state prefers to sit on the terminal hydroxo, which is needed to deprotonate the incoming water, rather than on a  $\mu^3$ -oxo. By introducing a step edge, the  $\mu^3$ -oxo becomes a much more basic  $\mu^2$ -oxo so that the proton stays on this site, leaving the terminal hydroxo free to deprotonate the water. The (311) surface is the simplest surface that contains such a step edge. This is described in detail in our JACS paper.<sup>2</sup>

The site on the (311) surface is sub-optimal because the oxygen atom that deprotonates the water and the oxygen atom that forms the hydroperoxo product have different proton affinities. The former is part of an  $\eta$ -hydroxo, the latter is a  $\mu^3$ -oxo. To improve the activity, one needs to increase the proton affinity of the  $\mu^3$ -oxo so that it is closer to that of the  $\eta$ -hydroxo. One way to do this may be to replace the Co(II) cation coordinating the  $\mu^3$ -oxo with a less acidic cation, although I am not sure what a good candidate would be.

1 M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362.

2 C. P. Plaisance and R. A. van Santen, *J. Am. Chem. Soc.*, 2015, **137**, 14660–14672.

**David Willock** continued: Your calculated barriers always seem to have a maximum point at the crossover point between different electronic states. Does this mean that the electron jumps before the proton moves in your PCET process or is more interpretation required?

**Craig Plaisance** answered: The electron jumps when the proton is approximately in-between the two oxygen atoms. The reaction coordinate in this part of the plot is mostly associated with the motion of the proton between the two oxygen atoms.

**Bert Weckhuysen** remarked: You provide us with new insights from theoretical chemistry. I am not so familiar with this field but what is the experimental backing/information to make the statement that one out of thousands are behaving in this way? What experiments are done to support this finding/conclusion?

**Craig Plaisance** answered: The experiments of Frei and coworkers<sup>1</sup> measured the turnover frequency of the active site by measuring the lifetime of an isotopically labeled superoxo intermediate detected by FTIR. The turnover frequency was found to be about 150 times greater than the rate per exposed Co on a nm-sized catalyst and 2500 times greater than the rate per exposed Co on a  $\mu\text{m}$ -sized catalyst.

1 M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362.

**Charles Campbell** enquired: I read that paper by Frei<sup>1</sup> to which you referred, where he simply divides the steady state rate per unit area by the first-order rate constant for a single elementary step to estimate the site density to be  $1/1000^{\text{th}}$  of the full surface area. I do not accept the logic of his analysis. At steady state, when one solves a microkinetic model for such reactions, one often finds such small ratios as being simply due to the presence of other adsorbates which block most of the active sites at steady state. When they are temporarily occupied in such a way, they cannot make a product, but that does not mean they are not active sites.

1 M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362.

**Craig Plaisance** replied: What you are saying is correct in principle, but I do not think this is how Frei and coworkers<sup>1</sup> determined the active site density. They

divided the steady state rate per unit area by the turnover frequency of the active site, not by the first-order rate constant for a single elementary step. The low active site density is supported by the 16-fold increase in rate per unit surface area they observe on a nm-sized particle vs. a  $\mu\text{m}$ -sized particle, indicating a high degree of structure sensitivity. While on the  $\mu\text{m}$ -sized particle, about 1/2500 surface sites are active, on the nm-sized particle, about 1/150 surface sites are active.

1 M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362.

**Neil Robinson** said: An interesting parallel between the mechanisms at the three sites you have studied is the role of surface hydroxyl groups in 'directing' the approach of water molecules through the formation of hydrogen bonding interactions. Such surface-adsorbate interactions are of course ubiquitous in many real-world catalytic systems due to the wide ranging coverage of surface hydroxyls on many catalytic materials and supports.

You have noted within the Introduction of your work (DOI: 10.1039/C5FD00213C) that only a very small number of active sites are responsible for the overall activity of such a catalyst. One might therefore expect some degree of competition to arise between the formation of hydrogen bonds with these active hydroxyls and with passive hydroxyls decorating the rest of the oxide surface. Do you believe any such competitive process will impact the kinetics of your reaction mechanism? Have you, for example, investigated the energetics of water adsorption to passive hydroxyls on the cobalt oxide surface in order to ascertain whether this adsorption competition has relevance from an adsorption energy point of view?

**Craig Plaisance** responded: I do not think that adsorption of water on the other hydroxyls will have a large effect on the TOF. A water molecule hydrogen bonding to these other hydroxyls will not block another water molecule from binding to the hydroxyls at the active site. There may be small perturbations due to changes in the complex network of hydrogen bonding in the solvent, but I do not expect these to be large.

**Christian Reece** enquired: In your model you use the microsolvation model to account for the effect of the solvent in your reaction, have you tried increasing the complexity of your model? Perhaps using dynamics to simulate the effect of a solvent? Do you feel that 'frozen' DFT simulations are still applicable when we know that a catalyst surface is a highly dynamic system?

**Craig Plaisance** answered: No, we have not tried a more complex solvation model as of now. We plan in the future to model the electrolyte using an implicit solvation model based on the Poisson-Boltzmann equation. Molecular dynamics is very expensive using DFT and hybrid QM/MM methods are rather involved to parameterize correctly, so these implicit solvation models are a good compromise.

As to the second question, I want to make a distinction between the dynamics related to solvent motion and the dynamics related to changes in the morphology of the catalyst particle. I believe that for surface catalytic reactions, transition state theory gives a good approximation of the rates of elementary processes.

Therefore, we can calculate these rates using statistical sampling rather than dynamics. In relation to solvent interactions, this would entail calculating the transition state free energy by sampling over many solvent configurations, while keeping the surface and adsorbates in the same local saddle point. This can be done using techniques such as thermodynamic integration and metadynamics. Even these techniques are very expensive, however, limiting their large-scale application such as in screening studies.

Concerning dynamics related to changes in the morphology of the catalyst particle, these processes happen on much longer timescales than the surface reactions that govern activity and selectivity. An active site will turn over many times before any changes in its structure can occur. Therefore, I believe that it is a very good approximation to treat the active site as a static entity. There is still, however, a very large distribution of different active sites on the catalyst particle which would require statistical sampling for a rigorous treatment.

In my work (DOI: 10.1039/C5FD00213C), I am more interested in using theory to understand how the structure of an active site influences its activity and selectivity, not so much about calculating a TOF for the entire catalyst particle. This allows us to determine the optimal active site for a given reaction. Once this is known, the question then becomes how can we maximize the number of these optimal active sites on a given catalyst particle.

**Michail Stamatakis** opened a general discussion: Catalysis is a multiscale problem and at each scale there exists a variety of modelling methodologies which we need to choose from. For instance, at the molecular scale one has several options of both static and dynamic approaches (DFT, configuration interaction, coupled cluster, *ab initio* MD, classical MD, *etc.*) At the catalyst scale one can formulate mean-field micro-kinetic models or carry out kinetic Monte Carlo (KMC) simulations. Dr Roldan made a choice to perform micro-kinetic modelling instead of KMC, and Dr Manganas chose the restricted open shell configuration interaction singles instead of other *ab initio* approaches. Are there any general guidelines on how we choose the most suitable approach for a system, given the complexity, and what information we need to obtain?

**Dimitrios Manganas** responded: As is stated in the second discussed paper (DOI: 10.1039/C5FD00193E), in order to successfully apply the theoretical spectroscopy approach it is of utmost importance that the theoretical methods are properly calibrated, meaning that the error bars of the theoretical predictions must be known from studying a series of known and understood systems. Hence, all predictions of the theoretical methods are only valid within the confidence intervals defined by the calibration procedure. All contemporary calculations of homogeneous and heterogeneous systems likewise are inflicted with methodological errors and those errors stem from the inevitable oversimplification of the real systems. It is for this reason that one is well advised to connect the theory with as many spectroscopic experiments as one can possibly obtain. It should be emphasized that, once a broad agreement between the theory and experiment has been achieved, one can: a) cross correlate the structure/spectra relationship between vastly different experimental methods and b) obtain experimentally calibrated insight into not only the geometric- but also the all-important electronic structure of the systems under investigation. The latter is instrumental for

obtaining deep insight into the reactivity of the system. The theoretical treatment of surfaces and solids is strongly dominated by the method of density functional theory (DFT). While this method has definite and important strengths and advantages, it also suffers from some significant shortcomings, as will be elaborated below. In particular, the field of L-edge spectroscopy cannot be successfully approached on the basis of DFT at all. Hence, our theoretical approaches deviate strongly from the currently employed DFT methods in that they are largely based on ideas from wavefunction-based *ab initio* quantum chemistry. We emphasize the properties of the N-particle states of the system (N being the number of electrons) in favour of the ubiquitous one-particle (orbital) picture that is implied by interpretation based on DFT. The drawback of focusing on wavefunction approaches is that truly periodic calculations are not available for the approaches that we are using. The next best alternative, that we follow, is to employ embedded clusters. Once the clusters are sufficiently large, the results of the periodic calculations are approached. However, convergence with cluster size is an issue that must be carefully monitored. Fortunately, cluster calculations with a few hundred atoms are feasible with modern hard- and software technologies, such that the limitations of using cluster models are not nearly as severe as they were in the past.

With all this in mind we have recently introduced the restricted open shell configuration interaction singles (ROClS) method as a method of general applicability to interpret metal L-edge spectra of a large class of molecules, ranging from mononuclear complexes up to polymetallic clusters.<sup>1-5</sup>

1 M. Roemelt and F. Neese, *J. Phys. Chem. A*, 2013, **117**, 3069.

2 M. Roemelt, D. Maganas, S. DeBeer and F. Neese, *J. Chem. Phys.*, 2013, **138**, 204101.

3 D. Maganas, M. Roemelt, M. Havecker, A. Trunschke, A. Knop-Gericke, R. Schlögl and F. Neese, *Phys. Chem. Chem. Phys.*, 2013, **15**, 7260.

4 D. Maganas, M. Roemelt, T. Weyhermüller, R. Blume, M. Havecker, A. Knop-Gericke, S. DeBeer, R. Schlögl and F. Neese, *Phys. Chem. Chem. Phys.*, 2014, **16**, 264.

5 D. Maganas, S. DeBeer and F. Neese, *Inorg. Chem.*, 2014, **53**, 6374.

**Alberto Roldan** also replied: Atomistic simulation is helpful to determine certain parameters of materials and catalysts. However, similar to characterisation techniques, there are different levels of calculations to determine, for instance, the electronic structure of a catalyst or the dynamic formation of a solid-liquid interface. Therefore, the selection of a particular atomistic technique depends on what you wish to analyse, similar to the choice between, for example, XPS and TEM to characterise a sample.

**Bruce Garrett** addressed Craig Plaisance, Alberto Roldan and Dimitrios Maganas: Calculations start with the definition of the structural model of the system. The structural models are always approximations of the system probed experimentally and should represent configurations contributing to the observable of interest. These configurations can include different sites on a catalyst that may have different compositions (*e.g.*, the presence or absence of lattice vacancies) as well as changes for a single site (*e.g.* those induced by thermal fluctuations of the geometry). It is possible that the most stable structures are not the ones that contribute the most to the experimental signal. For example, for reactive processes it is the transition state with the lowest free energy of activation and not

the equilibrium geometry with the lowest free energy that will contribute the most to the rate. What evidence do you have that your structural models are really representative of the ensembles contributing to the property of interest?

**Dimitrios Manganas** answered: As it is stated above, with no doubt, safe interpretations for a particular catalytic center can only be provided when spectra under operando conditions are collected and reaction intermediates through accurate energetic studies are identified. However, the scope of the present study (DOI: 10.1039/C5FD00193E) is a bit more fundamental, targeting spectra-structure correlations on catalytically relevant systems. The goal was to develop a combined experimental and theoretical protocol that involves a) state of the art experimental techniques such as multiwavelength Raman and multimetal soft X-ray spectroscopies and b) theoretical methods with strong predictive performance, that are applied in combination. In fact, combined experimental and theoretical multi-method protocols have been used to great advantage in (bio) inorganic chemistry and catalysis to unravel otherwise unknown structural topologies in enzymes (*e.g.* the identification of a unique carbide center in the active site of the dinitrogen activating enzyme nitrogenase), or in clarifying the structure and oxidation states of the oxygen evolving complex in photosynthesis (see references in the text of the manuscript). Hence in this study (DOI: 10.1039/C5FD00193E), a systematic computational protocol based on advanced theoretical spectroscopy was applied in order to extract the structural information of catalytically relevant centers, in both homogenous and heterogeneous catalysis. Certainly, as it is also stated in the conclusions, in the field of heterogeneous catalysis a universal structural identification of the catalytic center is a much more complicated task as there are additional factors that strongly influence the predominant structure of the active catalytic center, such as the support environment and the reaction conditions. In fact, in the case of silica supported vanadia catalysts, it has been shown that with a different support to SBA-15 and at certain conditions, a monomeric structure can dominate. Nevertheless, in our view, having a tool with such a high predictive capability forms an excellent basis for the design of dedicated spectroscopic experiments.

**Craig Plaisance** responded: In our study (DOI: 10.1039/C5FD00213C), we examined several active sites with very different structures and calculated the turnover frequency for each of them. Only one of these sites is present on the thermodynamically most stable (001) surface while another is present on a step edge defect. This latter site gives a calculated turnover frequency within 1–2 orders of magnitude of the experimentally measured value while the other sites have much lower turnover frequencies at the experimental overpotential. Furthermore, on this particular site, both water addition and O<sub>2</sub> release are calculated to be kinetically relevant, in agreement with the transient kinetics of a superoxo species observed in experiments.

More important than identifying the active site operating during the experiment, however, is to understand how the structure of the active site influences its activity. These kinds of questions are what theory is best at answering. Once we know what is the optimal active site, we can then try to synthesize a catalyst with a large number of these active sites.

**Alberto Roldan** also responded: We agree that the definition of the model is crucial for a reliable description of the catalyst. For this reason, a computational study requires as much experimental input as possible or needs to explore different options, *e.g.* when a reaction mechanism occurs on an idealised extended surface, it is not representative of the kinetics, as defects such as steps or vacancies should be considered as well.

**Richard Catlow** asked: Yours (DOI: 10.1039/C5FD00186B) and the other modelling papers show clearly the power of modelling in catalytic science. One crucial issue is the calculation of activation energies. Can you comment on the level of accuracy that we can now achieve, as accurate values are crucial if they are to be implemented in kinetic schemes?

**Alberto Roldan** answered: State-of-the-art computational methods allow the highly accurate calculation of energetics. However, the high accuracy often requires reducing the model size to a few atoms. Less accurate calculations, *e.g.* DFT, allow us to simulate more realistic systems and even include implicit/explicit solvents. These methodologies still provide reliable trends at an affordable cost and relatively short timescales.

**Andrzej Kotarba** addressed Craig Plaisance, Dimitrios Manganas, Alberto Roldan and David Willock: One of the important issues that I would like to point out is the adequate selection of the surface for molecular modelling that practical people deal with. More and more often we use DFT results to get molecular insights, to understand and interpret our experimental results. In this session we discussed the termination of  $\text{Co}_3\text{O}_4$  nanocrystals. The most probable facets and most often obtained experimentally are (100) and (111). (The DFT calculated surface energies of the facets increased in the following order  $1.39 \text{ J m}^{-2}$  (100) <  $1.48 \text{ J m}^{-2}$  (111) <  $1.65 \text{ J m}^{-2}$  (110).<sup>1</sup>) The calculations described in the paper (DOI: 10.1039/C5FD00213C) were done for (311) and (110). One of the experimental parameters that can be easily compared with the calculated one is the activation energy. Obviously, we measure the apparent activation energy, but still it can be compared with the highest activation barrier present in the calculated energetic profile. Shall we be satisfied when the difference between the theoretical and experimental values is below 10%? What are the other experimental parameters that can be directly calculated and compared to validate the theoretical model? Is it necessary to go into microkinetic modelling? How about the experimental average value of the electron work function, which we found as a good descriptor of the electrodonor properties of the catalytic surface (*e.g.* strong correlation with catalytic activity in a soot oxidation reaction)?

1 F. Zasada, W. Piskorz, P. Stelmachowski, A. Kotarba, J.-F. Paul, T. Płociński, K. Kurzydłowski and Z. Sojka, *J. Phys. Chem. C*, 2011, **115**, 6423.

**David Willock** responded: It is interesting to see that the DFT calculated surface energies give a nice rationale for the experimentally observed facets of real crystals. You are correct that, in calculations, we should consider the major facets but also the step edges that will be present as extended defects as these may have atomic geometries required for some reaction steps. In paper DOI: 10.1039/

C5FD00213C the (311) surface can be thought of as a periodic model of a step edge on the (111) facet of a real crystal. The ability of DFT and its modifications to recover exact values of the reaction barriers in surface reactions is still limited and an absolute accuracy of 10% should still be regarded as a good agreement. The power of modelling is to allow the effect of alterations to the surface composition and/or structure on the calculated barriers to be assessed, *i.e.* will a particular modification make the catalyst more or less efficient? Microkinetic modelling allows the overall kinetics of a chain of elementary steps to be evaluated and brings in the effects of site densities and non-Langmuir behaviour into play.

**Dimitrios Manganas** replied: As was also mentioned in this discussion, knowledge of reliable and quantitative experimental values for energetics, on as many steps as possible, along a catalytic cycle together with the key spectroscopic properties of the key reaction intermediates, offers significant information for a valid and useful theoretical study. This requires of course that the theoretical methods are properly calibrated against well-known systems.

**Craig Plaisance** also responded: I would like to point out that for the  $\text{Co}_3\text{O}_4$  system, the active site is very likely not on the most probable termination, as suggested by the results of Frei and coworkers,<sup>1</sup> which show that only 0.1–1% of the exposed sites are active. Thus, our active site on the (311) step edge is in good agreement with this high degree of structure sensitivity. In their experimental work, they do not determine an activation barrier but do determine a turnover frequency, which is within 1–2 orders of magnitude of the one we calculate on the (311) surface. I would consider this to be a very good agreement, especially considering that the TOF we calculate for the site on the more stable (001) surface is 3–4 orders of magnitude lower than on the (311) site at the experimental overpotential.

Other experimental parameters that could be compared are the kinetic orders with respect to reactant pressures/concentrations. Another one is the presence of reaction intermediates that are detected in the experiment. For example, Frei and coworkers<sup>1</sup> observe a superoxo intermediate using FTIR on  $\text{Co}_3\text{O}_4$ . The superoxo intermediate will also have a large concentration on the (311) active site since its formation is thermodynamically favorable and the reaction which consumes it ( $\text{O}_2$  release) is kinetically relevant at the experimental overpotential. This is not the case for any of the other active sites we studied.

Concerning microkinetic modelling, I think this becomes necessary whenever the reaction network is too complex to analyze ‘on paper’. For the OER, this is not the case since it essentially consists of two kinetically relevant steps occurring in series. Cycles with many branch points (Fischer Tropsch, for example) are probably too complicated to analyze on paper and require microkinetic modelling to identify the dominant pathways and kinetically relevant steps.

1 M. Zhang, M. de Respinis and H. Frei, *Nat. Chem.*, 2014, **6**, 362.

**Alberto Roldan** replied: Different computational approaches may provide very good agreement with the experimental values, although they are intensive and demanding. We should therefore compromise between accuracy and practicality without losing reliability. DFT calculations usually provide acceptable



energy values and can define adequate trends on the behaviour of the catalyst. There are many experimental parameters to compare with, from atomic distances and geometrical analysis to spectroscopy techniques such as infrared, XPS, *etc.* and certainly the electron work function is a clear, standard comparison between experiments and electronic structure calculations.

**Nicola Collis** addressed Craig Plaisance and Alberto Roldan: To what extent do you consider defects in a surface? We know that surface defects are important factors for both metal particle–support interactions in supported catalysts and surface reactivity in general so modelling perfect surfaces doesn't really capture the whole story of catalyst behaviour in real systems. All of the defects are important, oxygen vacancies and terminations (imperfect coordination at edges and corners) play a big role in the nature of the final catalyst.

**Craig Plaisance** answered: One of the active sites that we examine is located on a step edge and we find that this site gives the highest turnover frequency at intermediate overpotentials. I would imagine that oxygen vacancies are not present to a large extent in these systems because they are operating at a very high positive potential. Cation defects are likely to be more common as  $\text{Co}_3\text{O}_4$  is known to be a p-type semiconductor. These defects certainly play a role in the electrical conductivity which is vital to the overall performance of the catalyst, although it is beyond the scope of the current study. It may be interesting to examine the effect of cation defects near the active site in future studies.

**Alberto Roldan** replied: We agree on the important effect of defects in heterogeneous catalysis and it has been shown that low-coordinated atoms present a different activity than extended surfaces.<sup>1</sup> Nevertheless, defects are localised situations and extended surfaces are the starting point of an investigation if experimental data are not available to identify the catalytic site.

1 S. S. Tafreshi, *J. Phys. Chem. C*, 2014, **118**, 26103.

**Annette Trunschke** addressed Alberto Roldan and Craig Plaisance: Generally, it is assumed that only a small number of sites at the surface of a heterogeneous catalyst are active and responsible for catalysis (concept originally proposed by Sir H. S. Taylor in 1925). These sites exist in a non-balanced state (*e.g.*, low-coordinated species, defects, strained configurations). Theory tends to model the catalyst surface by minimizing the total energy of the considered system. In this way the thermodynamic equilibrium is taken into account, but metastable configurations are neglected. It has been shown, however, that high-energy sites account for catalytic activity. How does theory deal with metastable states at catalyst surfaces? Is it possible to use deviations from the thermodynamically stable state as another descriptor for catalytic activity?

**Craig Plaisance** answered: Generally, I think it is better to use theory to try and understand the relationship between the structure of the active site and its activity and/or selectivity, rather than use it to calculate a turnover frequency for a specific catalyst. This type of study brings a conceptual understanding that can lead to principles for designing the optimal active site for a given reaction. Once we

identify the structure of the active site giving the optimal theoretical performance, whether it be a low energy structure or a metastable defect site, we can try to synthesize a catalyst having a maximum concentration of these sites.

**Alberto Roldan** also responded: Static modelling provides insights into the thermochemistry of a system, usually considering periodic methodologies and well-defined systems. However, many reactive sites are located in defective non-ideal surfaces making their computation demanding. Recent advances in computational methods have developed reactive interatomic potentials that allow us to explore larger systems, including defects and dynamic aspects of the catalytic site. It shows the trend in simulation methodologies to aim at closer agreement with experimental conditions. Hopefully one day we will be able to model, within affordable timescales, stable and metastable states along reaction pathways.

**Shelaka Gupta** addressed **Craig Plaisance**: Do the solvation models predict the activation barrier correctly in DFT compared to the gas phase? Compared to calculations in the gas phase in DFT, are the solvent phase calculations using implicit and explicit models correct? How accurate are these models?

**Craig Plaisance** replied: I am not sure what the phrase ‘compared to the gas phase’ means since an activation barrier with a solvent present will obviously not be comparable to the activation barrier in the gas phase. Thank you for the clarification, though I still do not understand why one would want to use gas phase calculations to evaluate the accuracy of solvation methods. If you are asking whether these calculations with the solvation methods are more accurate than those in the gas phase, then yes, I would expect them to be more accurate. I do not have a great deal of experience using these solvation methods, however, so this is just my impression.

As far as the more general question “Do the solvation models predict the activation barrier correctly in DFT?”, I would say that good solvation models can accurately capture the electrostatic and dispersion interactions between the solute and the solvent. What they cannot capture accurately is hydrogen bonding. This is because these solvation models are based on a dielectric screening model, while hydrogen bonding is a chemical phenomenon involving the transfer of electron density between the solute and solvent. One way to better capture the effects of hydrogen bonding is to include the first shell of solvent molecules in the simulation and use the implicit solvent model to approximate the remainder of the solvent. This way, we model these hydrogen bonds explicitly while the implicit solvation model takes care of the interactions between the explicit solvent molecules and the bulk solvent. If the implicit solvent model accurately predicts the free energy of solvation of the solvent molecule (*e.g.* a water molecule solvated in water), then one can probably assume that the interactions between the explicit solvent molecules and the implicit solvent are accurate.

**Joachim Sauer** commented: Knowing the atomic structure of a solid catalyst in its as prepared form is an important first step in understanding heterogeneous catalysis. For enzymes, every mechanistic understanding started from the availability of an X-ray structure. With solid catalysts it is more difficult because

morphological defects and point defects may play a very important role. Care must be taken, however, when postulating defects in computational models. It is obvious that the reactivity of defects is higher. Therefore, the computations must include the full catalytic cycle with the regeneration of defects as the active site.

**Alberto Roldan** replied: We do agree with this comment. I would like to add that the information exchange between the experiment and the model is very important as it reduces the number of possible defects or structures to simulate, hence accelerating the outcomes.

**Rutger van Santen** remarked: To predict catalyst performance computationally remains a large challenge. One of the issues is best paraphrased as: ‘the snake bites its tail’. During reaction conditions the surface becomes in contact with adsorbate. The surface is typically highly covered with the adsorbate. This causes substantial lateral interactions, that are difficult to model and to include in microkinetics modelling. Also, these lateral interactions may induce surface reconstruction, which implies that catalytic reaction centers are added or destroyed. Such longer time events require the inclusion of instantaneous interactions of many particles at long length and time scales that can now only be done using molecular dynamics force field approaches, that are not yet very precise. The temperature of a reaction is also strongly dependent on the adsorption energies of the co-reactants, since the surface phase may alter during the reaction and depends on the reaction conditions. Proper simulation requires an iteration process of reactivity prediction, computation of altered local conditions due to product formation and recalculation of the surface phase.

Advances in the molecular understanding of heterogeneous catalyst reactivity are momentous and are due to advances in theory, spectroscopy and catalyst preparation. Currently, we are at the stage where the complexity of the interplay of catalytic reactivity events can become addressed.

**Michail Stamatakis** answered: Combining cluster expansions with Brønsted–Evans–Polanyi (BEP) relations is emerging as a successful approach for addressing the challenge of lateral interactions and their effects on kinetics (still on static surfaces though, no reconstructions).<sup>1</sup> Cluster expansion Hamiltonians are used to model in detail the energetics of the adsorbate overlayer, providing a way to calculate the energy for the initial and final state of a reaction in the presence of spectators. Then, BEP relations correlate the activation energy with the reaction energy (the latter computed by the cluster expansion), thereby providing a way to make the connection with kinetics. My lab has implemented this approach in an on-lattice kinetic Monte Carlo framework,<sup>2</sup> which has recently been applied to understand coverage effects on the CO–O titration experiment on Pd(111).<sup>3</sup> The latter study provides an explanation of the observed half-order kinetics with respect to O at high temperatures on the basis of such coverage effects, rather than O-island formation as previously thought.

1 C. Wu, D. J. Schmidt, C. Wolverton and W. F. Schneider, *J. Catal.*, 2012, **286**, 88.

2 J. Nielsen, M. d’Avezac, J. Hetherington and M. Stamatakis, *J. Chem. Phys.*, 2013, **139**, 224706.

3 M. Stamatakis and S. Piccinin, *ACS Catal.*, 2016, **6**, 2105.

**Robert Madix** responded: Professor van Santen raises a very important point. Let me extend the conversation somewhat. It is now well known that metal atoms on surfaces form small cluster complexes with adsorbed atoms. For example, hydrogen atoms mobilize Ni atoms on Ni(110) *via* the formation of NiH<sub>x</sub> entities and oxygen on Ag(111) or (110) surfaces forms local surface 'oxides', even at low coverage. In these cases the species may be involved in hydrogenation or oxidation reactions, respectively. The extent to which this occurs is a matter of the relative time scale for the reaction encounter between the second reactant and the adsorbed species *vs.* the time scale for the formation of these complexes. Obviously, if one first adsorbs either hydrogen or oxygen and then adsorbs the second reactant, the complex phases will form prior to the reaction. However, if the reactants are present simultaneously in the steady state, reaction pathways involving the 'naked' adsorbed species and the complexed species will compete. To the best of my knowledge this question has received very little, if any, attention. It is of obvious conceptual importance.

**Alberto Roldan** also replied: Indeed, there is work ongoing to address some of these difficulties. I would like to point out also that the reactivity is directly linked to the electronic structure of the catalyst, *e.g.* the d-band centre. In combination with BEP, this allows us to extrapolate static energy profiles to similar systems (*e.g.* dopants or different metals), where the mechanism takes place along the same intermediates. These and similar approaches help us to shorten timescales from basic research to manufacturing as recognised by the European Commission and the National Research Council of US.<sup>1,2</sup>

1 *Nat. Mater.*, 2016, **15**, 365.

2 Integrated Computational Materials Engineering: A Transformational Discipline for Improved Competitiveness and National Security, Washington, DC: The National Academies Press; 2008.

**David Willock** commented: All researchers in catalysis have a working 'model' of how they think the system is working at the molecular level, this is how we decide which materials to test for a given reaction. Computer simulation is a way to test out these models through calculations alongside experimental work. It links the structural characterisation of the materials to the elementary steps that occur in the surface catalysed reactions, giving a potential energy surface with which to test the likely validity of our conceptual models.

**Avelino Corma** opened the discussion of the paper by Joachim Sauer: Regarding the Brønsted sites, in those systems, there should be a lot of silanol groups, have you considered that? In reality, when you have these systems you should have plenty of silanol groups. What do you expect from the calculations, considering your existing knowledge?

**Joachim Sauer** answered: The synthesized nano-sheets of ZSM-5,<sup>1</sup> of course, are terminated with silanol groups. We are running calculations on models for such sheets. The presence of the silanol groups turns out to be a challenge for optimizing the structures. The surfaces of the silica-bilayers I was discussing in my contribution feature only (hydrophobic) Si–O–Si bonds, similar to the internal surfaces of the pores of all-silica zeolites.

1 M. Choi, K. Na, J. Kim, Y. Sakamoto, O. Terasaki and R. Ryoo, *Nature*, 2009, **461**, 246.

**David Willock** remarked: It should be possible to calculate the acidity of the silanol defect site using the same methodology that you have presented here.

**Joachim Sauer** replied: Yes, it is.

**Michael Bowker** asked: Is the influence of the metal surface included in these calculations? Most importantly the metal conduction electrons will screen out charges on the oxide, and image charges will also be present in the metal.

**Joachim Sauer** replied: For the explicit calculations of the OH frequency shift on CO adsorption on the Brønsted sites we have compared the free standing film in vacuum with the film supported by the metal surface. There are only minor changes. Note, that there are only van der Waals' interactions between the film and the metal layer which means that the screening effects will be damped.

Let me also add that we use the dielectric considerations only for rationalizing the results that have been obtained by explicit DFT calculations. The analytical model can be set up by taking a different dielectric constant for the film into account, for details see our paper.<sup>1</sup>

1 M. Rybicky and J. Sauer, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27873.

**David Willock** commented: You mention the increased dispersion interaction between a molecule and the surface of a pore compared to a flat surface. The dispersion is increased because the molecule is effectively closer to a larger area of the surface. The pore will also restrict the configurations available to the molecule, particularly as the dimensions of the pore approach the kinetic diameter of the molecule. So although the enthalpy of adsorption becomes more negative, the entropy of the molecule will also become less positive and so the effect of the pore structure on the free energy of adsorption is more difficult to predict.

**Joachim Sauer** replied: It is the loss of translational (and rotational) entropy of the gas that counteracts the energy gain on adsorption, and the balance of the two terms for specific pressure and temperature determines the adsorption equilibrium. Indeed, on a flat surface the loss of translational entropy will be less.

I have discussed energy effects only. There are two that go in opposite directions: On the flat film, stabilization of the adsorbate by dispersion is less because of the missing pore fit. On the contrary, the intrinsic binding strength may be higher because of a higher acidity which is due to the smaller dielectric constant of the thin film.

**Viet Thang Ho** asked: You investigated Brønsted acidity of 2D and 3D systems based on the effective dielectric constant and this parameter dependence is lower in 2D than in 3D systems, what are the effects of the thickness of the 2D material on the dielectric constant? Have you investigated the Brønsted acidity of 2D zeolites on different materials, for example MFI or MCM-22 zeolite?

**Joachim Sauer** replied: The thinner the layer the smaller the effective dielectric constant.<sup>1</sup> So far we have done calculations for 2D systems only on the hexagonal double layer described in our paper (DOI: 10.1039/C5FD00207A). There are calculations in progress for ZSM-5 thin sheets as experimentally studied.<sup>2</sup>

1 M. Rybicki and J. Sauer, *Phys. Chem. Chem. Phys.*, 2015, 17, 27873.

2 Y. Seo, K. Cho, Y. Jung and R. Ryoo, *ACS Catal.*, 2013, 3, 713.

**Charles Campbell** remarked: Regarding the last comment: Since the zeolite is an insulator, I assume that the charge screening length is much, much longer than the film thickness you are modelling.

**Joachim Sauer** replied: Indeed, the difference between the bulk materials and thin films will only show up if the film thickness is below the screening length.

**David Willock** continued: We have had quite a discussion on the representation of the dielectric constant of materials in the type of computer model that you use. Do the materials discussed in your paper (DOI: 10.1039/C5FD00207A) have particularly high dielectric constants?

**Joachim Sauer** answered: The dielectric constant for the bulk zeolite (2.9) is close to or somewhat above the values reported for dense silica polymorphs, e.g. 2.4 for  $\alpha$ -quartz.<sup>1</sup> Our average value for the thin film (1.8) is significantly lower, and this is the very point in my discussion.

1 L. Levien, C. T. Previtt, D. J. Weidner, *Am. Mineral.*, 1980, 65, 920.

**Richard Catlow** enquired: You point out that in general the absolute deprotonation energy is not a good measure of acidity, but in the case of the results on the SAPO system which you presented, there is clearly a correlation. Can you comment on the circumstances or systems for which the deprotonation will be a useful guide to acidity

**Joachim Sauer** replied: The deprotonation energy probes the final state of the reaction. It will be a useful measure, only if the interaction of the probe molecule in the initial state and the protonated molecule in the final state are negligible or cancel. This is expected to be the case for a similar local surface environment (SAPO-34 and SSZ-13 both have the CHA structure), but not if this environment is as different as between a planar surface (2-dimensional film) and a cavity. For gas phase molecules, there is no interaction and the deprotonation energy is generally used as a measure of acidity.

**Itai Panas** commented: We learned about the change in acidity when going from a zeolite bulk to a supported two-layer structure, and that crucial to the resulting acidity is the polarizability of the solid acting as a 'solvent' to the remaining charge on deprotonation. Upon performing periodic boundary condition calculations, inter-unit cell repulsion (owing to the translational symmetry) between intra-unit cell induced dipoles (monopole contribution removed) should act to artificially suppress the deprotonation. Was any dependence of acidity on supercell size (coverage) observed for the freestanding two-

layer system? If so, would it be expected that a metallic support would act to reduce this effect?

**Joachim Sauer** responded: For the free-standing silica bilayer we have performed calculations for different cell sizes,<sup>1</sup> and the effective dielectric constant has been derived from a plot of the calculated deprotonation energy as a function of the inverse distance between the charges created on deprotonation. We did not do such calculations in the presence of the metal substrate, but we expect changes compared to the free standing film. The changes may turn out to be modest, because the distance between the silica bilayer and the metal support is in the range of van der Waals' bonds.

1 M. Rybicki and J. Sauer, *Phys. Chem. Chem. Phys.*, 2015, **17**, 27873.

**Viet Thang Ho** opened the discussion of the paper by Alexander O'Malley: There are 12 different T sites in MFI zeolite, how can you choose 3 representative T sites in your study? This means that you cannot conclude the acidity of MFI is lower than that of FAU zeolite. Also, I disagree completely with your results of the deprotonation energies without considering the stability of the Brønsted site at each Al position because the lowest deprotonation energies are not always the most stable Brønsted sites.

**Alexander O'Malley** replied: The number of symmetry inequivalent Brønsted sites in MFI is, in fact, significantly higher as the interaction between Al substituted T sites as well as differing proton positions result in numerous configurations and disorder (the full unit cell is also twice as large and low *T*NMR clearly shows a larger number of T sites).<sup>1,2</sup> The most stable, *i.e.* the lowest energy, Brønsted sites will necessarily have the highest deprotonation energy. Energy distribution of Al over a number of zeolitic frameworks has been the subject of numerous previous investigations reported in the literature.<sup>3,4,5</sup> Importantly, in the real material, Al siting would most probably be controlled by kinetic factors that are determined by the history of any particular sample, including the synthesis method and post-synthetic treatments, but not their thermodynamic stability. In particular, proton forms of zeolites often obtained by ion exchange in metal zeolites (*e.g.* Na or K), where siting of the extraframework cations has a crucial effect on the preferential siting of framework Al, has also been previously studied computationally.<sup>6</sup> Despite the plethora of possibilities, the sites of interest would most significantly differ in their local environment and accessibility by guest molecules, with the basic mechanism of acidic catalysis shared by 'similar' sites. From this point of view it is entirely reasonable to pick and investigate representative active sites, which has been done in our study (DOI: 10.1039/C6FD00010J), and is common practice in this field.

We emphasise that deprotonation energies are not a direct measure of acidity of respective Brønsted sites and are indeed only one factor amongst several that contribute to the acidity of a site.

1 C. A. Fyfe, J. H. O'Brien and H. Strobl, *Nature*, 1987, **326**, 281.

2 S. Sklenak, J. Dedecek, C. Li, B. Wichterlova, V. Gabova, M. Sierka and J. Sauer, *Phys. Chem. Chem. Phys.*, 2009, **11**, 1237.

3 K. P. Schröder, J. Sauer, M. Leslie and C. R. A. Catlow, *Zeolites*, 1992, **12**, 20.

- 4 R. Grau-Crespo, A. G. Peralta, A. R. Ruiz-Salvador, A. Gómez and R. López-Cordero, *Phys. Chem. Chem. Phys.*, 2000, **2**, 5716.
- 5 G. Sastre, V. Fornes and A. Corma, *J. Phys. Chem. B*, 2002, **106**, 701.
- 6 S. A. French, R. Coates, D. W. Lewis and C. R. A. Catlow, *J. Solid State Chem.*, 2011, **184**, 1484.

**David Willock** remarked: Your models of the adsorption of methanol to the zeolite surface suggest a significant methyl C-H interaction with the oxygen basic sites. Did you try to calculate the barrier to methyl rotation in these structures to estimate the degree to which this is hindered by these interactions?

**Alexander O'Malley** answered: We did not explore the rotational barrier of methyl groups interacting with basic oxygen sites. However, this development would be a sensible extension of our work (DOI: 10.1039/C6FD00010J) in assessing the strength of C-H interactions with the framework. The rotation of the methyl group would be hindered by the Brønsted acid site and the nearby framework as noted by Prof. Sauer, and torsional interactions with the methanol O-H would also affect the rotational barrier. The study of methyl rotation barriers is possible experimentally through NMR and techniques based on quasielastic neutron scattering, which can then be compared to computed values and so would be suitable complementary methods for future investigations.

**Michael Bowker** asked: As in the vein of Prof Sauer's paper (DOI: 10.1039/C5FD00207A), this is an atomic scale simulation, with a small spatial extent, so is the screening length factor embedded in the calculation or does it not matter? As the dielectric constant is a bulk measure is it not an appropriate factor in such calculations which operate on the nanoscale? Surely at this level a 'local dielectric constant' is both different and directional?

**Alexander O'Malley** answered: The approach both we and Prof. Sauer use describes the dielectric response including any anisotropic components, fully using an atomistic model for all regions near the charged species that are created. As a large region is modelled atomistically, the response of the remaining distant regions will be small and can be handled by a correction based on a continuum dielectric model

**Richard Catlow** commented: Regarding the calculation of the deprotonation energy, this is best considered in terms of the creation of a charged defect with the energy being determined largely by the electrostatic energy of the interaction of the charge on the defect (in this case the negatively charged deprotonated species) and the surrounding lattice with the (stabilising) polarisation energy, *i.e.* the dielectric response of the lattice.

**Joachim Sauer** commented: In our calculations, we explicitly included everything at the atomic level, *i.e.*, we performed supercell calculations with an increasing distance between the negatively charged defects. We then fitted an analytical expression that includes the dielectric constant<sup>1</sup> and obtained our effective values for the dielectric constant. That means the dielectric constant does not enter our results, it is rather used to rationalize the numeric results.



1 M. Leslie and M. J. Gillan, *J. Phys. C: Solid State Phys.*, 1985, **18**, 973.

**Cynthia Friend** opened the discussion of the paper by Jakub Staszak Jirkovský: Did you consider and/or measure compositional changes as the pH or the potential changed? It is possible, even likely, that composition at the surface changes and the state of the material is not necessarily at equilibrium.

**Jakub Staszak-Jirkovský** answered: These are important questions for the analysis of the electrocatalytic properties of alloys. There are several effects that can be foreseen. These are related to changes in the surface segregation of Pd due to the adsorption of OH and/or oxygenated species, to the stability of surface oxides/adsorbed oxygenated species and to the reduction mechanisms itself. The segregation energies of Pd in a Au host for bulk phases<sup>1</sup> and nanoparticles<sup>2</sup> calculated under vacuum are 0.28 and 0.89 eV per atom, respectively, *i.e.*, the replacement of a surface Au atom by Pd should be unfavourable. It is well established, however, that this behaviour is radically altered by the binding of adsorbates to alloy components. For Au<sub>1-x</sub>Pd<sub>x</sub> nanoalloys, electrochemical measurements showed that Pd atom surface segregation leading to oxide formation is only observed for nanoalloys with  $x > 0.15$ , whereas no significant oxide phase formation was observed at lower Pd concentrations at potentials more negative than 0.2 V *vs.* SCE.<sup>3</sup> Regarding the possibility of non-equilibrium conditions in the nanoalloys investigated, previous work showed that indeed, there is an asymmetry in the rates of Pd oxidation from the nanoalloy due to the formation of surface oxides with the corresponding abstraction of Pd atoms from the bulk of the nanoparticles and the reduction. The rate of abstraction of Pd to the surface is very fast but its re-incorporation rate to the bulk is slow.<sup>4</sup> The origin of this asymmetry is not clear but to avoid uncertainties in the composition, the electrodes used in this work (DOI: 10.1039/C5FD00233H) were never poised at potentials where Pd oxide formation could take place ( $E > 0.6$  V *vs.* SCE) that could result in hysteresis effects due to the irreversibility of oxide reduction. As an additional measure, the scans from which the rate constants have been calculated always started at the negative end, just before hydrogen evolution, to ensure that the measurements corresponded to a reduced surface.

For comparison purposes, all the present work (DOI: 10.1039/C5FD00233H) was carried out at the same acid concentration, 0.1 M HClO<sub>4</sub>. In experiments with nanoalloys, care has to be taken to ensure that oxide adsorption does not take place in the potential range of interest to avoid large Pd concentration changes and this introduces a severe limitation on the pH at which the measurements can be carried out. Thus, increasing the solution pH reduces the available potential range where oxide-free surfaces can be investigated.

1 A. V. Ruban, H. L. Skriver and J. K. Nørskov, *Phys. Rev. B*, 1999, **59**, 15990.

2 L.-L. Wang and D. D. Johnson, *J. Am. Chem. Soc.*, 2009, **131**, 14023.

3 J. S. Jirkovský, I. Panas, E. Ahlberg, M. Halasa, S. Romani and D. J. Schiffrin, *J. Am. Chem. Soc.*, 2011, **133**, 19432.

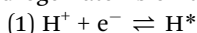
4 J. S. Jirkovský, I. Panas, S. Romani, E. Ahlberg and D. J. Schiffrin, *J. Phys. Chem. Lett.*, 2012, **3**, 315.

**Cynthia Friend** continued: Under the reaction conditions, you may have metastable phases present, not only the thermodynamic phases. Have you considered this possibility and considered how you might model them?

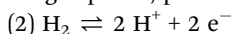
**David Willock** replied: If we have structures for the metastable phases then we should be able to simulate them in the same way as any other structure. The difficulty is estimating the relative importance of the thermodynamically preferred and the large number of possible alternative structures. Experiments can help here if we have some structural information on the active form of the catalyst.

**Craig Plaisance** asked: In your talk, you mentioned some of the similarities and differences between electrochemical and non-electrochemical H<sub>2</sub>O<sub>2</sub> production. Do you think there is fundamentally any difference between these processes at the microscopic level?

More specifically, consider we have a non-electrochemical system with an H<sub>2</sub> pressure exactly equivalent to the operating potential of the electrochemical system with respect to the SHE and occurring at the same pH. In both of these systems, the following equilibrium is present between the protons in solution, hydrogen atoms on the metal surface (H\*), and electrons in the metal bulk:



In the non-electrochemical system, we also have the equilibrium between H<sub>2</sub> in the gas phase, protons in solution, and electrons in the bulk metal:



In the electrochemical system, this reaction can be considered to occur in the reference electrode. Fundamentally, it does not seem like it would matter whether reaction (2) occurs on the catalyst surface or in the reference electrode. This would give identical chemical potentials of H<sup>+</sup> and e<sup>-</sup> in the two systems, and therefore, identical H\* concentrations on the catalyst surface.

**Jakub Staszak-Jirkovský** responded: There are two considerations here. The thermodynamics for the overall potential determining reaction is as you describe in equation (2) and the role of H\* in the reduction of O<sub>2</sub> to peroxide subsequently in reaction (1). The rate of the chemical reaction following the Horiuti–Polanyi (H–P) hydrogenation mechanism<sup>1</sup> will depend both on the surface coverage by adsorbed hydrogen (M–H) and hence, on the Gibbs energy of reaction (1), and on the Gibbs energy of the reaction of H\* with O<sub>2</sub> (or O–OH\*). Electrochemical hydrogen adsorption (termed Hupd in electrochemical literature), however, does not take place on Au and no surface hydride adsorbed film can be detected on gold surfaces.<sup>2,3</sup> In spite of this, the electrochemical reduction of O<sub>2</sub> on both bulk<sup>4</sup> and nanoparticulate gold<sup>5</sup> does lead to the production of peroxide with significant yields without any evidence of the presence of Hupd on the electrode surface. Thus, in these cases, the prevalent electrochemical mechanism involves electron transfer from the nanoparticle's Fermi level to the oxygen species, either adsorbed or in solution, and not hydride transfer. The chemical and electrochemical mechanisms are dissimilar. Although for the Au–Pd alloys the surface coverage by H\* at the active sites will be the same regardless of the way the potential is applied, the rate determining steps for hydride and electron transfer are very different. The former requires H<sub>2</sub> dissociative adsorption followed by M–H bond breaking, whereas the latter implies electron transfer. In this respect, mechanistic considerations are important to decide how to investigate possible improvements to alternatives, if any, to the current anthraquinone production method. At potentials close or below 0 V against the reversible hydrogen electrode (that

correspond to the potentials where reaction (2) occurs reversibly) there could be an overlap between the electrochemical and heterogeneous mechanism. At these potentials,  $H^*$  can exist at the surface and the reaction could proceed *via* a similar mechanism as in the heterogeneous case. The difference, however, is that in electrochemical systems electrons can travel through the external electrical circuit, whereas in heterogeneous systems this cannot happen. In order to preserve charge balance, both oxidation and reduction reactions must take place at the same rate, akin to a corrosion process. Please also note that in the electrochemical case only oxygen reduction reactions prevail at the Au–Pd electrode.

- 1 I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, 1934, **30**, 1164.
- 2 M. A. Rizatti and K. Jüttner, *J. Electroanal. Chem.*, 1983, **144**, 351.
- 3 A. Hamelin and A. M. Martins, *J. Electroanal. Chem.*, 1996, **407**, 13.
- 4 T. Inasaki and S. Kobayashi, *Electrochim. Acta*, 2009, **54**, 4893.
- 5 J. S. Jirkovský, M. Halasa and D. J. Schiffrin *Phys. Chem. Chem. Phys.*, 2010, **12**, 8042.

**Michael Bowker** enquired: Do you know your surface composition, and do you know what kind of surface you want? What is the role of Pd? Presumably it is in the surface in order to dissociate the oxygen?

**Jakub Staszak-Jirkovský** responded: We comment on the surface composition in our reply to the question from Dr Cynthia M. Friend. The overall aim was to obtain a catalytic material that could be incorporated into a fuel cell so as to allow the partial use of the Gibbs energy of the oxygen reduction reaction to generate electricity, thus providing a route for a co-generation process where the electrical energy produced would appear as a hydrogen peroxide production credit. Our original idea was to obtain metallic electrocatalytic alloy surfaces containing metal centres (the so-called ‘hot spots’<sup>1</sup>) that would provide sites for the end-on adsorption of oxygen, since this geometry would lead naturally to the electrochemical reduction of oxygen to peroxide. Pd was an obvious choice, although DFT modelling indicated that Pt–Au alloys would be equally satisfactory. However, due to the risk of catalytic decomposition of the peroxide produced by Pt, Pd was used throughout as the gold alloying element. The role of Pd was to provide the single atom catalytic centre for  $O_2$  binding that would result in an appropriate ensemble for the central reaction sequence described in this paper (DOI: 10.1039/C5FD00233H), thus avoiding the dissociation of the O–O bond on further reduction to produce water.

- 1 J. S. Jirkovský, I. Panas, E. Ahlberg, M. Halasa, S. Romani and D. J. Schiffrin, *J. Am. Chem. Soc.*, 2011, **133**, 19432.

**Cynthia Friend** said: Although you assert that there are isolated, single Pd atoms, that has not been demonstrated. A single Pd atom may not be sufficient. I understand that you base your assertion on that Pd is isolated, because you do not observe behavior indicating that PdO forms. On the other hand, small clusters of Pd can still have oxygen bound to them, but not form an oxide. Did you consider other possible configurations of Pd in the catalyst and specifically calculate the free energy? It is likely that there is a distribution of Pd configurations and arrangements that may contribute to various extents.

**Jakub Staszak-Jirkovský** answered: We did not attempt to measure the surface concentration of Pd monomers but relied on abundant literature information of the well-known properties of Au–Pd alloys. It has been known for a long time that these alloys have unusual surface properties and in particular, that ensembles involving Pd monomers, in contrast with those containing neighbouring Pd atoms, are the most stable. This property is important for understating the strong dependence of catalytic activity on alloy composition. The evidence for this has been obtained from a variety of techniques. From STM measurements, Behm *et al.*<sup>1</sup> demonstrated that monoatomic ensembles predominate in the low Pd concentration range (7 and 15%). Goodman *et al.*<sup>2</sup> confirmed these results employing low-energy ion scattering spectroscopy (LEISS), infrared absorption spectroscopy (IRAS), temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS) and concluded that these are responsible for the observed catalytic properties of these alloys.<sup>3,4</sup> More recent STM studies by Baber *et al.*<sup>5</sup> have also demonstrated that Pd monomers constitute the most stable configuration for dilute Au–Pd alloys.

Many modelling studies of this important catalytic system confirm these experimental observations. The energetically favourable presence of Pd monomers in Au–Pd alloys compared with those of dimer or trimer ensembles has been demonstrated from first principles calculations by Jacob *et al.*<sup>6</sup> and by Yuan *et al.*<sup>7</sup> The role of Pd monomers in Pd@Au ensembles for the direct H<sub>2</sub> + O<sub>2</sub> peroxide synthesis has been highlighted by Ham *et al.*<sup>8</sup> employing DFT calculations and showing the effect of a surface Pd atom selectivity in preserving the integrity of the O–O bond during hydrogenation.

Previous work on similar electrocatalysis showed that for Au and Pd, both surface oxides and adsorbed oxygenated species are electrochemically reduced at the potentials investigated for O<sub>2</sub> reduction (see Fig. 4 in ref. 9 DOI: 10.1039/C5FD00233H). Although we agree that other ensembles could be present in our experiments, at a low concentration of Pd nanoalloys, their surface concentration is very likely to be small not only for the reasons presented above but also due to the peroxide yields observed for the low Pd concentration nanoalloys. The presence of vicinal surface Pd atoms leads to water formation and hence decreases the peroxide yield, in agreement with the experimental observations in the present work (DOI: 10.1039/C5FD00233H) for increasing concentrations of Pd in the nanoalloys investigated.

1 F. Maroun, F. Ozanam, O. M. Magnussen and R. J. Behm, *Science*, 2001, **293**, 1811.

2 C.-W. Yi, K. Luo, T. Wei and D. W. Goodman, *J. Phys. Chem. B*, 2005, **109**, 18535.

3 M.S. Chen, K. Luo, T. Wei, Z. Yan, D. Kumar, C.-W. Yi and D.W. Goodman, *Catal. Today*, 2006, **117**, 37.

4 M. Chen, D. Kumar, C.-W. Yi and D. W Goodman, *Science*, 2005, **310**, 291.

5 A. E. Baber, H. L. Tierney and E. C. H. Sykes, *ACS Nano*, 2010, **4**, 1637.

6 S. Venkatachalam and T. Jacob, *Phys. Chem. Chem. Phys.*, 2009, **11**, 3263.

7 D. Yuan, X. Gong and R. Wu, *Phys. Rev. B*, 2007, **75**, 085428.

8 H. C. Ham, G. S. Hwang, J. Han, S. W. Nam and T. H. Lim, *J. Phys. Chem. C*, 2009, **113**, 12944.

9 J. S. Jirkovský, I. Panas, E. Ahlberg, M. Halasa, S. Romani and D. J. Schiffrin, *J. Am. Chem. Soc.*, 2011, **133**, 19432.

**Michael Bowker** opened a general discussion: We must believe in scientific approach and in our ability to accurately measure properties experimentally, and to predict them from theory. Using theory, we can, in the future, tackle the design

of new catalysts. If we identify the intermediates and their binding energies (TPD spectroscopy), and the barriers to conversion at the rate determining step (*e.g.* using TPD or molecular beam methods), and plug these numbers into microkinetic models, then we can prescribe the improvement in rate for that particular step. This could be by, for example, the decreasing of the binding of a critical intermediate. In turn, theory could establish whether this would happen for a different metal, or in the presence of 'poisons' or promoters, for the experimentalist to then verify. I believe these kinds of developments are just around the corner.

**Joachim Sauer** remarked: I do not believe in *in silico* design of new catalysts, I believe in the powerful computational methods and tools we have today when used in close collaboration with experimental techniques. 'Theory' is behind both experiment and computation. An important issue is the relevance of the computational models for the experiments performed. The question has been raised why can't computational chemistry be more predictive for catalytic reaction steps.

Within the limitations of the Born–Oppenheimer approximation, stable structures are the local minima on the potential energy surface and we have methods to find the global minimum structures, *e.g.* genetic algorithms. Because of the errors connected with the existing methods for calculating the potential energy surface, these structures need to be verified by experiments. We also have methods of statistical thermodynamics which allow us to predict the most stable phases under given external conditions (partial pressure) and for a given temperature. The situation is much less favorable for transition structures between minima which define the elementary reaction steps.

We are missing general techniques for identifying all possible elementary reaction steps from a given intermediate, which means that we do not have the methods for a complete exploration of the whole reaction mechanism.

Again, feedback loops between computational predictions and experiments are necessary. There are developments in the right direction, *e.g.* the work of Maeda, Taketsugu, and Morokuma.<sup>1</sup>

1 S. Maeda, T. Taketsugu and K. Morokuma, *J. Comput. Chem.*, 2014, **35**, 166.

**Richard Catlow** continued: I agree with you that *in silico* design is not a useful concept. We use modelling together with experiment to develop a molecular understanding of catalysis. It is worth noting, however, that global optimisation methods are now very effective at predicting both bulk and surface structures.