DISCUSSIONS

Advanced approaches: general discussion

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Naomi Lawes, David Lennon, Diyuan Li, [ID] Patrick Morgan,
Andrea M. Oyarzún Aravena, [ID] Christian Reece, Romain Réocreux,
Peter W. Seavill, [ID] Yasushi Sekine, Mzamo Shozi, [ID] Ian Silverwood, [ID]
Mikhail Sinev, Collin Smith, Michail Stamatakis, Laura Torrente
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Simon Kondrat opened discussion of the paper by Valerii Bukhtiyarov: The influence on butene selectivity by using metal acetate precursors is very interesting. Your work and findings remind me of previous work by myself and others on the influence of heat treatment atmosphere on the final metal compound, particularly the influence of oxygen partial pressure.[1,2] We found high partial pressure and a replenishing environment, *i.e.* high flows, resulted in low carbon deposits and oxide formation, although this is metal dependent. Low partial pressures resulted in partial reduction of metals and some carbonaceous formation. While inert environments facilitated reduction to metal and the formation of carbon overlays or in the case of palladium even metal carbide formation.[2]

In catalyst synthesis could you try variation in oxygen exposure to influence your Rh/C surface ratio? This might further alter your reaction selectivity and provide more insight for the mechanism of butadiene hydrogenation? Perhaps very high oxygen flow rates might remove the carbon totally? Lastly, have you seen any evidence of Rh carbide?

1 S. A. Kondrat, *et al.*, *J. Catal.*, 2011, **281**, 279, DOI: 10.1016/j.jcat.2011.05.012.
2 S. A. Kondrat, *et al.*, *Chem. Sci.*, 2012, **3**, 2965, DOI: 10.1039/c2sc20450a.

Valerii Bukhtiyarov answered: We have thoroughly checked the catalyst preparation procedure. Firstly, we have started with titanium dioxide, Hombifine N ($S_{BET} = 103$ m^2 g^{-1}) was used as the support. The TiO$_2$ samples were calcined at 550 °C for 2 h prior to use and then dried at 120 °C for 6 h. Then, two series of the

Rh/TiO$_2$ catalysts were prepared with the variation of several different preparation parameters.

Two catalysts were prepared by incipient impregnation (0.8 mL g^{-1}) of dry TiO$_2$ by the calculated amount of rhodium nitrate or acetate solution. The materials were then dried in air at 120 °C for 3 h, and calcination of the impregnated support in the air at 600 °C for 2 h followed by the reduction in H$_2$ flow at 330 °C for 3 h finalized the preparation procedure. For the third catalyst, binuclear acetic rhodium(II) complex [Rh$_2$(OAc)$_4$] (preparation procedure is described in ref. 1) was used as the precursor. The catalyst was prepared by incipient impregnation of dry TiO$_2$ with [Rh$_2$(OAc)$_4$] solution in ethanol, then the solvent excess was evaporated at 40 °C at reduced pressure. The subsequent calcination/reduction treatment was the same as described above. So we used air flow for calcination and do not vary the flow rate. Furthermore, we cannot really measure the Rh/C ratio with XPS, because the concentration of Rh was small (1 wt%), and carbon was distributed not only on rhodium particles, but also on the support. The conclusion about the presence of carbon on the rhodium particle surface was made on the basis of the different behavior of the Rh dispersion determined with CO adsorption and the mean particle size measured with TEM.

1 R. S. Drago, R. Cosmano and J. Telser, *Inorg. Chem.*, 1984, **23**, 3120–3124.

Matthew Conway communicated: Were experiments conducted where the support was calcined at these temperatures before the Rh was added? Could this enhancement be due to the removal of residual sulfur/chlorine from the support?

Valerii Bukhtiyarov communicated in reply: The support was calcined at 600 °C before the rhodium was added by impregnation. We can see that the calcination decreases by two times the specific area due to enlargement of initial TiO$_2$ crystallite. So such impurities such as sulfur or chlorine should be removed before the catalyst preparation and cannot be the reason of variation of catalytic properties.

Naomi Lawes asked: In your paper (DOI: 10.1039/c9fd00138g) you mentioned the rapid deactivation of Rh/TiO$_2$_CC, have you performed post reaction characterisation to investigate the difference in stability?

Valerii Bukhtiyarov responded: Unfortunately, we have no real investigation of the deactivation process. But high resistance of Rh particles against sintering (see TEM data of Fig. 6 in the paper (DOI: 10.1039/c9fd00138g)) indicates that enlargement of Rh particles is rarely a reason for deactivation. Therefore, we can conclude that new carbonaceous residues produced from butadiene or the intermediates of its hydrogenation can cause the deactivation.

Graham Hutchings enquired: With the parahydrogen-induced polarization (PHIP) effect is it possible to investigate the partial hydrogenation of substituted acetylenes with Pd and PdAg catalysts to try to get an insight in the reaction mechanism by which the triple bond can be hydrogenated and not the resulting double bond?

Valerii Bukhtiyarov answered: I think this is a good idea. Moreover in our recent paper[1] we have shown that both bimetallic PdAu alloy and Au shell–Pd core particles prepared by deposition of metals on highly oriented pyrolytic graphite (HOPG) support demonstrate 2–5 orders of magnitude higher activity in pairwise hydrogen addition in selective hydrogenation of propyne in comparison with the monometallic Pd sample. The enhanced selectivity of bimetallic samples in pairwise hydrogen addition can be explained by the reduced mobility of hydrogen atoms on the catalyst surface leading to preservation of spin correlation between the protons. The reduced mobility of H atoms, in turn, is caused by Pd isolation by inactive in hydrogenation Au atoms on the surface, *i.e.* by the disruption of continuous Pd ensembles by gold. Of course, for detailed study of reaction mechanisms we should prepare and investigate a number of such catalysts with variation of the Pd/Au ratio and preparation procedure.

1 A. V. Bukhtiyarov, D. B. Burueva, I. P. Prosvirin, A. Y. Klyushin, M. A. Panafidin, K. V. Kovtunov, V. I. Bukhtiyarov and I. V. Koptyug, *J. Phys. Chem. C*, 2018, **122**, 18588.

Deniz Uner asked: The data from parahydrogen enhanced spectra is very clearly revealing the reaction pathway. Do you have information from ^{1}H NMR spectroscopy about the surface species, on the active phase and on the support?

Valerii Bukhtiyarov replied: Unfortunately, the signal from surface species has so low intensity that they are not seen in ^{1}H NMR spectra.

Deniz Uner queried: Is there a possibility to pursue parahydrogen induced signal enhancement protocols in NMR spectroscopy to elucidate the interactions of the surface bound species, for your reaction/catalyst system?

Valerii Bukhtiyarov responded: To answer this question, we should take into account two points: (i) low concentration of the rhodium particles supported on the high surface area TiO_2 (1 wt%), and (ii) low concentration of the surface species compared with concentration of molecules in the gas phase. Both these points make it impossible to register the surface species with NMR spectroscopy. Moreover, our attempts to make this in recent investigation of propyne hydrogenation over Pd and Pd–Au particles supported on highly oriented pyrolytic graphite,[1] when the surface concentration of the metal deposited on the planar support is much higher than in the case of the Rh/TiO_2 catalysts used in this paper, were unsuccessful.[1]

1 A. V. Bukhtiyarov, D. B. Burueva, I. P. Prosvirin, A. Y. Klyushin, M. A. Panafidin, K. V. Kovtunov, V. I. Bukhtiyarov and I. V. Koptyug, *J. Phys. Chem. C*, 2018, **122**, 18588.

Matthew Conway asked: At the temperature used in your experiments, the equilibrium proportion of parahydrogen should constitute 25% of the mixture as the ortho form is more stable.[1] Have you measured the rate of para- to ortho-hydrogen conversion? Could the real proportion of the pairwise route be hidden by failing to take this into account and the observed differences between materials be attributed solely to the differences in rate of spin isotope equilibration?

1 G. C. Bond, *Catalysis by metals*, Academic Press, London, 1962.

Valerii Bukhtiyarov replied: The initial fraction of parahydrogen in the H_2 gas is 90.5%. Once the gas contacts the catalyst, this value starts to decrease toward the equilibrium value of 25%. However, under our experimental conditions this process is relatively slow and cannot significantly affect the results and the conclusions of the work. Unlike parahydrogen which gives no NMR signal, orthohydrogen can be readily seen in the ^{1}H NMR spectra. For instance, its signal can be discerned in the blue trace in Fig. 1 in the paper (DOI: 10.1039/c9fd00138g) as a broad feature centered at about 4.8 ppm. However, the intensity of this broad signal is significantly lower than what we observe for normal hydrogen (25% parahydrogen + 75% orthohydrogen). This tells us that the parahydrogen fraction does not decrease significantly from its initial value of *ca.* 90%. Furthermore, it can be seen that in the spectra of Fig. 3 the orthohydrogen signal is essentially not visible, which confirms that in these experiments the back conversion of parahydrogen is negligible. The main reason for slow re-equilibration of H_2 spin isomers is the continuous supply of the fresh gas mixture to the reaction zone with a flow rate sufficiently high to maintain the parahydrogen fraction close to initial levels.

Ali Reza Kamali said: Thank you for presenting this interesting work! I have a question/comment. In this work, you have used rhodium nitrate and acetate as the precursors of rhodium. The first one has nitrogen in it and the second one carbon. The production process also involves high temperature heat treatments. Two possibilities that might occur here are doping of TiO_2 by nitrogen/carbon, and also the dissolution of nitrogen/carbon in rhodium, which may influence the catalytic activity of the catalysts. Perhaps your XPS results also show the presence of these elements. I am wondering whether you have looked at these possibilities at all?

Valerii Bukhtiyarov replied: Thank you very much for your question. I agree that application of rhodium nitrate and acetate precursors can result in doping the catalyst surface with nitrogen and carbon. But we tried to control these processes with XPS. XPS shows that no nitrogen is presented inside the XPS sensitivity limit. The amount of carbon can be estimated from Table 1 presented in the paper (DOI: 10.1039/c9fd00138g). The samples using rhodium nitrate or acetate as precursors have similar content of carbon, but the application of binuclear $[Rh_2(OAc)_4]$ complexes as precursor increases the C/Ti ratio by two times indicating the presence of additional carbon on the catalyst surface. Moreover, we have used this fact to explain high selectivity in hydrogenation of butadiene to butene, but not to butane, by the formation of specific sites on the rhodium particles under the influence of additional carbon.

Matthew Conway enquired: Can you comment on how or when the strong metal–support interaction (SMSI) state forms for the calcined at 600 °C? This state typically only forms under >450 °C in a hydrogen atmosphere and the chemisorption results in Table 2 in the paper are higher than what would be expected if this were the case.[1] Moreover, recent work by Hutchings and co-workers suggests

that for Pt/TiO$_2$ catalysts the formation of the SMSI state can be eliminated by a calcination prior to a reductive treatment.[2]

1 T. W. van Deelen, C. Hernández Mejía and K. P. de Jong, Control of metal–support interactions in heterogeneous catalysts to enhance activity and selectivity, *Nat. Catal.*, 2019, **2**, 955–970.
2 M. Macino, A. J. Barnes, S. M. Althahban, *et al.*, Tuning of catalytic sites in Pt/TiO$_2$ catalysts for the chemoselective hydrogenation of 3-nitrostyrene, *Nat. Catal.*, 2019, **2**, 873–881.

Valerii Bukhtiyarov responded: I agree that in our case we have no classical SMSI effect appearing as a result of high temperature reduction of the catalysts, which apply reducible oxide (TiO$_2$, CeO$_2$, *etc.*) as support. The reduction reduces the support and reduced species, for example TiO$_x$, covers partially active metal particles. And indeed, subsequent oxidative treatment removes this effect *via* reversible oxidation of the reduced species of the supports. Further reduction returns the catalyst to the initial state. However, this procedure can create a new, more active state of the catalyst. Indeed, as mentioned in the cited Hutchings' paper,[1] the following calcination treatment with reduction (both at 450 °C), allowed them to prepare an exceptionally active catalyst. Detailed characterization has revealed that the peripheral sites at the Pt/TiO$_2$ interface are the most likely active sites for this hydrogenation reaction. If we return to our experiments, I would like to mention that initial calcination of TiO$_2$ before rhodium impregnation at 550 °C decreases the specific surface area by two times mostly due to enlargement of the support crystallites. Application of even higher temperature for the Rh/TiO$_2$ catalyst calcination (600 °C) can cause further transformation of the support structure with the formation of larger amounts of specific sites (maybe at the Pt/TiO$_2$ interface) which exhibit higher activity in pairwise hydrogen addition (Fig. 5 in the paper).

1 M. Macino, A. J. Barnes, S. M. Althahban, *et al.*, Tuning of catalytic sites in Pt/TiO$_2$ catalysts for the chemoselective hydrogenation of 3-nitrostyrene, *Nat. Catal.*, 2019, **2**, 873–881.

Philip Davies questioned: What do you think are the most important differences between the nitrate and acetate prepared catalysts? What is it about the nitrate route that gives rise to the different catalyst? I note that whilst the dispersion is a little greater, the XPS gives a Rh concentration almost three times greater – is this because of flatter nanoparticles perhaps?

Valerii Bukhtiyarov replied: I suggest that the most important differences between the nitrate and acetate prepared catalysts is the amount of carbon residues deposited on the rhodium particle surface. The higher concentration of carbon in the case of the acetate samples results in, for example, higher selectivity in hydrogenation of butadiene to butene. In the case of the catalyst prepared *via* the nitrate route, the main difference is observed for the sample calcined at 600 °C – this sample is characterized by higher pairwise addition of hydrogen. Our explanation of this fact is transformation of the support structure with the formation of the larger number of specific sites (maybe at the Pt/TiO$_2$ interface) which exhibit higher activity in pairwise hydrogen addition (Fig. 5 in the paper). I cannot understand the last note, because we have no information that the XPS gives rise to a Rh concentration almost three times greater. Table 2 in the paper shows that such change (three times) is observed only for the dispersion determined with CO

adsorption for the Rh/TiO$_2$ sample calcined at 600 °C, but the XPS signal from rhodium (Rh/Ti atomic ratio) is varied by 30% only. These data lead us to the conclusion that rhodium particles are blocked partially by TiO$_2$ creating the special sites active in pairwise hydrogen addition both to propyne and to butadiene. So, the conclusion about flatter Rh nanoparticles has no experimental basis.

Shaoliang Guan said: XPS has clearly shown the ratio changes of different elements before and after reaction. I'm wondering if there's any change in the oxidation states of specific elements, such as Rh. It would be nice to see actual XPS spectra in the paper or supplementary information.

Valerii Bukhtiyarov responded: In this paper, XPS spectra were measured after transferring the Rh/TiO$_2$ samples to the spectrometer through the atmosphere. This procedure oxidizes the rhodium partially, so that the Rh 3d spectrum consists of two components – metallic rhodium with binding energy of 307.4 eV and Rh$_2$O$_3$ species with binding energy of 309.2 eV, with ratio of Rh to Rh$_2$O$_3$ varying from 5 : 1 to 3 : 1 depending on the time of contact with the atmosphere. Typical Rh 3d spectra from similar Rh/TiO$_2$ samples have been published by us earlier.[1] So, for the purpose of this paper we have presented and analyzed only quantitative XPS data – the ratio of Rh to Ti.

1 D. B. Burueva, O. G. Salnikov, K. V. Kovtunov, A. S. Romanov, L. M. Kovtunova, A. K. Khudorozhkov, A. V. Bukhtiyarov, I. P. Prosvirin, V. I. Bukhtiyarov and I. V. Koptyug, *J. Phys. Chem. C*, 2016, **120**(25), 13541–13548.

Ali Reza Kamali opened discussion of the paper by Andrew Beale: Thank you Professor Beale for your nice work and presentation! I am curious whether you have done any electron microscopy analysis to further investigate the morphology and distribution of various phases in the catalyst? An analytical TEM/STEM analysis may also help for the characterisation of new tungsten phases you have observed.

Andrew Beale answered: Thank you for you comment/question. We have performed scanning electron microscopy (SEM) on these samples but not TEM/STEM. The SEM does reveal some morphological information and some variation in the distribution of some of the elements in the catalyst formulation. Some TEM characterisation work has been published by others on these materials and it doesn't look like they were able to reveal too much more.[1] I agree though that further detailed and higher spatial resolution EM studies are warranted and that these could provide greater insight into the nature of these W-containing species. However, in our work (DOI: 10.1039/c9fd00142e) we do show how the catalyst undergoes quite extensive change during activation and reaction so in an ideal world, the TEM/STEM should be performed in similar circumstances in order for some more definitive structure–activity relationships to be obtained. As the reaction proceeds at very high temperatures this will be rather challenging.

1 J. Kim, L.-H. Park, J.-M. Ha and E. D. Park, *Catalysts*, 2019, **9**, 363, DOI: 10.3390/catal9040363.

Mikhail Sinev asked: In your paper (DOI: 10.1039/c9fd00142e) it is said that the W species are directly involved in the catalyst active site responsible for CH_4 conversion. Could you please clarify whether the tungsten-containing moieties are directly responsible for the activation of methane, or they provide an optimal environment for the species that directly activate it?

Andrew Beale responded: Alas with the data that we have it is difficult to differentiate the roles of the various species present. Certainly W-containing catalysts have been shown to be able to generate high C_2 yields even without the presence of the elements also present here, so it seems that it has a particular capacity for methane activation.

Mikhail Sinev said: The main result of the work is that you improve the catalyst durability by applying a special thermal treatment. What is physical nature of this effect? Does your volatile component (sodium tungstate) become less volatile thermodynamically? Or for some reason, after such treatment, the sublimation becomes slower, *i.e.* is it a kinetic effect?

Andrew Beale answered: The thermal treatment has been shown to change the NaWO-speciation, leading to more Na–W–O–Si species and also evidence for similar species containing Mn has also been observed. So we rationalise that the transformation of the Na_2WO_4 phase is critical for mitigating volatility.

David Lennon enquired: When considering the catalyst under reaction conditions (Section 3.2; DOI: 10.1039/c9fd00142e) you state that the catalyst active components are present in the form of a molten state but that this phase is not detectable with X-ray diffraction. However, can your impressive *operando* imaging methodology provide information for the onset of the molten state? For example, do the diffraction linewidths for the incident Na_2WO_4 and Mn_2O_3 phases show systematic trends as the temperature is increased and the molten state achieved?

Andrew Beale replied: Thanks for your question. Yes we do see the melting of the Na_2WO_4 at around 700 °C. This occurs quite suddenly so it is difficult to discern clearly a broadening of the reflection beforehand. The reflections due to Mn_2O_3 do become weaker in intensity and discernibly broader with time/temperature but these changes are less noticeable, especially since Mn_2O_3 reflections are still observable at 780 °C nominal as it doesn't melt at this temperature. So our take on this is that molten Na_2WO_4 reacts with crystalline Mn_2O_3 to form an active Na–Mn–W–O type species.

Ian Silverwood queried: You suggest that the active phase may be a liquid, but the images show well-defined particles that do not move during treatment. Is the suggestion that the liquid phase is confined to the surface of the solid? Is there any evidence for re-orientation in the sample either through melting or under the influence of gravity?

Andrew Beale responded: Thanks for your question. The particles comprise SiO_2 with Na_2WO_4/Mn_2O_3 deposited on them. It is the Na_2WO_4 phase that melts rather than the SiO_2 so yes indeed the Na_2WO_4 is confined to the surface. We do

see migration of the Na_2WO_4 but this seems mainly due to its volatility – this can be seen in Fig. 4 of our contribution (DOI: 10.1039/c9fd00142e).

Simon Kondrat asked: How important is the silica support in the evolution and stability of these molten phases? Is the silica a simple dispersant and therefore does only surface area matter? In that regard, why not start with quartz if this is the thermodynamically favoured phase under operating conditions?

Andrew Beale replied: In this case the silica is mainly present as a dispersant. It would be good to use quartz as the silica polymorph although generally this is only available in a low surface area form and hence would result in a catalyst with low dispersion and lower activity.

Ian Silverwood questioned: Your catalyst is immobilised between glass wool plugs in the quartz reactor at temperatures where the glass wool could soften and flow. Do you see any evidence for this?

Andrew Beale responded: Thanks for your question. We don't see evidence for softening of the quartz wool. This is probably because the heat source (hot air gun) to the reactor is unidirectional and therefore the heat is concentrated on the catalyst resulting in the quartz wool experiencing a lower temperature.

Michael Claeys enquired: The reactor depicted in Fig. 1 in the paper (DOI: 10.1039/c9fd00142e) seems to be open on top? Is it venting to atmosphere and external extraction takes care of those gases?

Andrew Beale replied: Thanks for your question. Yes, for the *operando* experiments the reactor is open at the top as at the time it was too challenging to acquire data on a sealed reactor (would lead to problems when reconstructing the data). The mass spectrometry line samples at the end of the catalyst bed. Indeed gas extraction/ventilation is placed above the reactor to ensure that the experimental hutch is well ventilated.

Michael Claeys asked: What if you were working with nastier gases or higher pressures – is there a "closed" version of the reactor?

Andrew Beale answered: Thanks for your question. Yes, we have commissioned a closed version of the reactor and tested this up to 4 barg. The first results obtained from this reactor were published in ref. 1.

1 S. W. T. Price, *et al.*, *Sci. Adv.*, 2017, **3**(3), e1602838.

Nico Fischer said: By varying the calcination conditions you observe changes in stability, activity and selectivity of your OCM catalyst. Interestingly, a longer calcination, under N_2 or air, seems to have comparable effects in terms of activity and stability but opposite effects on C_2 selectivity. Could you please elaborate on that?

Andrew Beale responded: Thank you for your question. From these data it is difficult to determine any causal link between the catalytic performance and the effects of the thermal treatments and the speciation as determined from the diffraction data. This is also complicated by the testing conditions not being directly comparable. There is almost certainly some link between the multicomponent (particularly concerning Mn/W speciation induced by air *vs.* inert gas treatment. Unfortunately due to severe Mn/W loss from the catalyst treated in air it is difficult to perform any further post reaction analysis in this regard.

Graham Hutchings remarked: In methane coupling using oxide catalysts at high temperature the greater majority of the observed data comply with what is known as the 100% rule. This is that the conversion and selectivity to C_2 products sum to at most 100%. This means that the maximum yield possible, if this rule holds will be 25%. However, you indicate a higher yield of *ca.* 30% in the research you report. In the previous studies where the 100% rule was observed, the reactions occurring are considered to be surface initiated gas phase radical processes. You indicate that during the reaction some of the catalyst is sublimed, is it possible that this sublimed material is also active?

Andrew Beale replied: Thank you for your question and observations Graham. Apologies for the confusion regarding the 30% ethylene yield claim. The project aimed, with membrane reactors, to achieve a 30% yield as this would render the process more economically viable. However, as you say, the data (which are only shown for the performance of the catalyst in the absence of a membrane) are some way off hitting that target. I am sure that the sublimed species will show some activity as this material comprises a NaWO 'polymorph'. However, it is almost certainly the case that the deposition occurs due to cooling downstream of the reactor and hence the temperature of the reactor at that point may not be hot enough to enable the oxidative coupling of methane (OCM) reaction to occur.

Mikhail Sinev asked: It is well known that product distributions in the OCM process dramatically change with conversion. You state that after the treatment the C_2-selectivity increases from 40 to 70%. Do these numbers refer to the same conversion?

Andrew Beale responded: In this work we kept the flow characteristics during catalytic reaction common across the different activation/reaction conditions as the work was benchmarking performance for a catalyst reactor with fixed operating conditions. So we don't report selectivities at similar conversions.

Megha Anand opened discussion of the paper by Aram Bugaev: The reaction starts with pure palladium and you observe formation of PdC during the course of the reaction. Is it understood why there is no loss of activity once the carbide is formed for hydrogenation of ethylene over palladium?

Aram Bugaev replied: First of all, it is not so obvious if the activity in ethylene to ethane conversion should be reduced or not. In this work (DOI: 10.1039/c9fd00139e) and in several previous studies[1–3] we observed not only that palladium carbide is an active catalyst, but also that the conversion is slightly reduced

before the carbide phase is formed. A similar effect was observed in the work of Zhao *et al.*[4]

Second, it should be noted that under the investigated conditions (1–10 mg 5% Pd/C catalyst, capillary-based flow-reactor 1 mm in diameter, 1 bar total pressure, temperature range 30–120 °C, ethylene and hydrogen flows in the 0–20 mL min^{-1} range) we observed almost full conversion of ethylene, which is not an optimal condition to follow the changes in the catalytic activity. The same full conversion was observed even if the catalyst was diluted 7 : 1 with carbon, when we were almost unable to collect any distinct XANES data.

1 A. L. Bugaev, A. A. Guda, I. A. Pankin, E. Groppo, R. Pellegrini, A. Longo, A. V. Soldatov and C. Lamberti, *Catal. Today*, 2019, **336**, 40–44.
2 A. L. Bugaev, O. A. Usoltsev, A. Lazzarini, K. A. Lomachenko, A. A. Guda, R. Pellegrini, M. Carosso, J. G. Vitillo, E. Groppo, J. A. van Bokhoven, A. V. Soldatov and C. Lamberti, *Faraday Discuss.*, 2018, **208**, 187–205, DOI: 10.1039/c7fd00211d.
3 A. A. Skorynina, A. A. Tereshchenko, O. A. Usoltsev, A. L. Bugaev, K. A. Lomachenko, A. A. Guda, E. Groppo, R. Pellegrini, C. Lamberti and A. Soldatov, *Radiat. Phys. Chem.*, 2020, **175**, 108079.
4 S. Zhao, Y. Li, D. Liu, J. Liu, Y.-M. Liu, D. N. Zakharov, Q. Wu, A. Orlov, A. A. Gewirth, E. A. Stach, R. G. Nuzzo and A. I. Frenkel, *J. Phys. Chem. C*, 2017, **121**, 18962–18972.

Dmitry Eremin asked: You showed great examples of changes in Pd–Pd distance and formation of carbide phase within a catalytic run and also how carbide is formed and accumulated from cycle-to-cycle upon recycling a catalyst. But how stable is the carbide phase if you stop the reaction, expose your catalyst to air and continue with it again? Will there be any difference in quantity of carbide or perhaps hydride as well?

Aram Bugaev answered: The carbide phase is formed quite irreversibly and is stable under various conditions[1–4] including exposure to pure hydrogen.[1,3] We did not test exposing the catalyst to air, but it could be expected that exposure to oxygen at high temperature may remove the carbide. The hydride phase is much better investigated and it is known that it decomposes rapidly (in few seconds for nanosized particles[5,6]) as soon as the partial hydrogen pressure is below that of palladium hydride formation at a given pressure.[7,8]

1 A. L. Bugaev, A. A. Guda, A. Lazzarini, K. A. Lomachenko, E. Groppo, R. Pellegrini, A. Piovano, H. Emerich, A. V. Soldatov, L. A. Bugaev, V. P. Dmitriev, J. A. van Bokhoven and C. Lamberti, *Catal. Today*, 2017, **283**, 119–126.
2 A. L. Bugaev, O. A. Usoltsev, A. Lazzarini, K. A. Lomachenko, A. A. Guda, R. Pellegrini, M. Carosso, J. G. Vitillo, E. Groppo, J. A. van Bokhoven, A. V. Soldatov and C. Lamberti, *Faraday Discuss.*, 2018, **208**, 187–205, DOI: 10.1039/c7fd00211d.
3 A. L. Bugaev, O. A. Usoltsev, A. A. Guda, K. A. Lomachenko, I. A. Pankin, Y. V. Rusalev, H. Emerich, E. Groppo, R. Pellegrini, A. V. Soldatov, J. A. van Bokhoven and C. Lamberti, *J. Phys. Chem. C*, 2018, **122**, 12029–12037.
4 O. A. Usoltsev, A. Y. Pnevskaya, E. G. Kamyshova, A. A. Tereshchenko, A. A. Skorynina, W. Zhang, T. Yao, A. L. Bugaev and A. V. Soldatov, *Nanomaterials*, 2020, **10**, 1643.
5 C. Langhammer, V. P. Zhdanov, I. Zoric and B. Kasemo, *Phys. Rev. Lett.*, 2010, **104**, 135502.
6 A. L. Bugaev, A. A. Guda, K. A. Lomachenko and A. V. Soldatov, *JETP Lett.*, 2019, **109**, 594–599.
7 A. L. Bugaev, A. A. Guda, A. Lazzarini, K. A. Lomachenko, E. Groppo, R. Pellegrini, A. Piovano, H. Emerich, A. V. Soldatov, L. A. Bugaev, V. P. Dmitriev, J. A. van Bokhoven and C. Lamberti, *Catal. Today*, 2017, **283**, 119–126.
8 A. L. Bugaev, A. A. Guda, K. A. Lomachenko, A. Lazzarini, V. V. Srabionyan, J. G. Vitillo, A. Piovano, E. Groppo, L. A. Bugaev, A. V. Soldatov, V. P. Dmitriev, R. Pellegrini, J. A. van Bokhoven and C. Lamberti, *J. Phys. Conf. Ser.*, 2016, **712**, 012032.

M. Bowker remarked: As you will know we have an abiding interest in carbide formation, and have worked on both catalysts and single crystals, and find similar carbidisation in ethene (and with a range of other molecules). In our work on catalysts what we see, in the absence of hydrogen, is rather different from your work in the presence of hydrogen. If we pass ethene over the catalyst, we do make the carbide, but by a disproportionation reaction in which C is deposited on the Pd and methane is evolved (*i.e.* $C_2H_4 \rightarrow CH_4 + C_{ads}$).[1] We see a similar lattice expansion to you with the formed bulk carbide. Do you see any methane formation? Can you estimate from your work x in the formula PdC_x, and justify the value you find? The literature generally suggests $x \sim 0.17$ saturation value (usually by reference to a very early estimate[2,3]), although this is often after rather low temperature reaction and rarely involves chemical titration of C uptake. We find that to saturate uptake takes temperatures of at least 500 K.

1 W. Jones, P. P. Wells, E. K. Gibson, A. Chutia, I. P. Silverwood, C. R. A. Catlow and M. Bowker, Carbidisation of Pd nanoparticles by ethene decomposition with methane production, *ChemCatChem*, 2019, **11**, 4334–4339.
2 J. A. McCaulley, *J. Phys. Chem.*, 1993, **97**, 10372–10379.
3 J. A. McCaulley, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1993, **47**, 4873.

Aram Bugaev responded: We did not observe any significant signal of methane in the mass spectrometry data both in the presence and in the absence of hydrogen. However, if only ethylene is sent we have seen by infrared spectroscopy formation of various intermediates indicating dehydrogenation of ethylene with formation of palladium carbides, confirmed by XAS, even at 50 °C.[1] So, the results are very much correlated to your findings.[2] The C/Pd ratio estimated by our method[3] is around 0.13,[3] which is close to the values reported in the literature. It should be noted that we always worked with *ca.* 3 nm nanoparticles, for which I would expect a lower C/Pd ratio than in the bulk palladium (analogously to Pd hydrides), and the maximal investigated temperature was 100 °C. However, this value should be treated with care for several reasons:

(i) The values were obtained from comparison between theoretical and experimental XANES spectra.

(ii) We are sensitive not only to C inside the Pd lattice but also to surface adsorbed hydrocarbons. Recently we have made several attempts to discriminate these contributions[3,4] but their effect on spectra is very similar.

1 O. A. Usoltsev, A. Y. Pnevskaya, E. G. Kamyshova, A. A. Tereshchenko, A. A. Skorynina, W. Zhang, T. Yao, A. L. Bugaev and A. V. Soldatov, *Nanomaterials*, 2020, **10**, 1643.
2 W. Jones, P. P. Wells, E. K. Gibson, A. Chutia, I. P. Silverwood, C. R. A. Catlow and M. Bowker, *ChemCatChem*, 2019, **11**, 4334–4339.
3 A. Martini, S. A. Guda, A. A. Guda, G. Smolentsev, A. Algasov, O. Usoltsev, M. A. Soldatov, A. Bugaev, Y. Rusalev, C. Lamberti and A. V. Soldatov, *Comput. Phys. Commun.*, 2020, **250**, 107064.
4 O. A. Usoltsev, A. L. Bugaev, A. A. Guda, S. A. Guda and A. V. Soldatov, *Top. Catal.*, 2020, **63**, 58–65.

M. Bowker added: Regarding the surface intermediates you propose, note that, at least on single crystal Pd(110), the main intermediate (most stable intermediate prior to total dehydrogenation) is the C_2H group that you also show in one of your figures.[1]

1 M. Bowker, C. Morgan, N. Perkins, R. Holroyd, E. Fourre, F. Grillo and A. MacDowall, Ethene adsorption, dehydrogenation and reaction with Pd(110): Pd as a carbon sponge, *J. Phys. Chem. B*, 2005, **109**, 2377–2386.

Justin Hargreaves asked: Thank you very much for your very informative presentation. If possible, please could you very kindly comment upon the electronic structure of the carbide/carbides you see in terms of Engel–Brewer theory, charge transfer or the appearance of their XANES spectra.

Aram Bugaev replied: The changes at *ca.* 24.37 keV in the shape of the first XANES maximum (see *e.g.* Fig. S4 and S6 of the ESI; DOI: 10.1039/c9fd00139e) are indicative of the new antibonding state formed due to the chemical bonding of Pd and C. On the other hand there is also a slight shift to the lower energies of the first maximum in the derivative of XANES spectra (see Fig. 1 here), which is associated with the absorption edge position. This may be explained by the fact that carbon is donating electrons to palladium.

Sarayute Chansai enquired: Can you comment on why you use 80 °C for this study? Is it optimised for the rate of carbide formation?

Aram Bugaev responded: We were trying to choose the lowest temperature possible at which we can initiate the phase transition from β-hydride to metallic palladium by tuning the flow of H_2 on the mass flow controller. For 20 °C, for example, this occurs at partial hydrogen pressure of *ca.* 20 mbar,[1] which means that at the total flow of 50 mL min^{-1} the hydride phase should form already at 1 mL min^{-1} of hydrogen. At 80 °C, the phase transition starts at *ca.* 100 mbar, and is also spanned over a bigger pressure interval (the full transition to β-hydride occurs above 300 mbar H_2), so we were able to gradually "drive" our catalyst through its different states by tuning the gas flows.
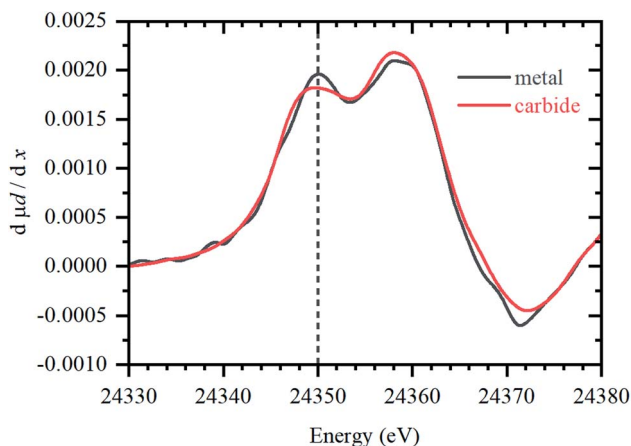

Fig. 1   First derivatives of the normalized XANES spectra for palladium nanoparticles in metallic (black) and carbide (red) phases.

1 A. L. Bugaev, A. A. Guda, K. A. Lomachenko, V. V. Shapovalov, A. Lazzarini, J. G. Vitillo, L. A. Bugaev, E. Groppo, R. Pellegrini, A. V. Soldatov, J. A. van Bokhoven and C. Lamberti, *J. Phys. Chem. C*, 2017, **121**, 18202–18213.

Sarayute Chansai added: Related to my previous question, did you think the temperature change would influence the formation of carbide in this reaction?

Aram Bugaev answered: Definitely. We have recently showed that both the rate of formation and the saturated values differ a lot in the process of carbide formation at 50 and 100 °C.[1]

1 A. A. Skorynina, A. A. Tereshchenko, O. A. Usoltsev, A. L. Bugaev, K. A. Lomachenko, A. A. Guda, E. Groppo, R. Pellegrini, C. Lamberti and A. Soldatov, *Radiat. Phys. Chem.*, 2020, **175**, 108079.

M. Bowker remarked: Two papers in this session have had some discussion of carbide formation during hydrogenation reactions.

I would like to comment about hydrogenation on transition metals generally and particularly for Pd (and late TM) catalysts which are widely used in organic molecule hydrogenations. I wonder if such catalysts are also carbidised during reaction, and it is actually this carbidisation that makes it a good catalyst, and better for ethene hydrogenation (Bugaev paper; DOI: 10.1039/c9fd00139e) than the pure metal. I propose that is generally the case for such reactions that the pure metal is a dehydrogenator (fast decomposition and C deposition), whereas the carbide is a more efficient hydrogenator.

Simon Kondrat added: A very general question to Mike and all regarding carbide phases in hydrogenation, how important are specific structures? For earlier transition metals Fe, Mo multiple carbide phases can form and the scientific discussion is a bit clearer as to there being specific phases that are "active".

For later transition metals, Pd, Rh, Ni, Ir for example. The phases are metals with interstitial carbon. How much carbon incorporation is good? How dynamic is this? Is a surface rich gradient of C insertion beneficial?

M. Bowker noted: The lattice expansion is not as big as you might expect for C interstitial in Pd. This could be due to charge transfer from Pd to C, and shift of the d-band away from the Fermi level – in turn this would alter the catalytic properties.

Aram Bugaev remarked: I would argue that the lattice expansion is not big, because we studied *ca.* 3 nm palladium particles and not the ideal crystal. For example, in the case of palladium hydrides, the lattice expansion and the estimated H/Pd ratio for the same particles were considerably smaller than those for bulk palladium.[1] Concerning the second part of the comment, I fully agree that changes in electronic structure of Pd atoms occur which should have an effect on the catalytic properties.

1 A. L. Bugaev, A. A. Guda, K. A. Lomachenko, V. V. Shapovalov, A. Lazzarini, J. G. Vitillo, L. A. Bugaev, E. Groppo, R. Pellegrini, A. V. Soldatov, J. A. van Bokhoven and C. Lamberti, *J. Phys. Chem. C*, 2017, **121**, 18202–18213.

Naomi Lawes opened discussion of the paper by Nico Fischer: You mentioned the exclusion of surface area and pore volume by adding the overlayers. What would happen to the catalytic behaviour if you were to explore these physical properties. In what way could this also influence the Fe/Ni surface state/alloy phase?

Nico Fischer responded: It is very important to note that the application of overlayers could well influence properties of the overlayer materials compared to their bulk counterparts, such as ion mobility, reducibility, *etc.* The idea behind the present study and ongoing experiments is to identify, amongst other insights, a correlation between catalyst activity/selectivity/stability and oxide layer properties. How this can be translated to bulk metal oxides as carriers remains to be seen.

What we avoid with this approach are uncertainties in the data stemming from different physical properties which can also affect the FeNi speciation. For example a lower BET surface area could result in increased sintering, smaller pores could get blocked by FeNi particles or C and different sized pores could also result in a varied interaction with the FeNi phase(s) in turn affecting reducibility and active surface area.

M. Bowker said: Bulk carbide formation is crucial in Fischer–Tropsch, as you know well. At the end of the paper (DOI: 10.1039/c9fd00139e), the TGA shows considerable weight loss (and therefore, if due entirely to C loss, considerable atomic wt% C). Can you tell us if you dismiss carbide formation for these systems?

Nico Fischer replied: At this stage we do not have any evidence for carbide formation. However we cannot fully exclude their presence in minor concentrations. Prior literature, especially from the group of Jingguang Chen (ref. 1 and citations within), have reported on similar Fe and Ni containing systems. With (*in situ*) XAS no evidence for carbides was found either.

1 Z. Xie, L. R. Winter and J. G. Chen, Bimetallic-derived catalysts and their application in simultaneous upgrading of CO_2 and ethane, *Matter*, 2021, **4**(2), 408–440.

M. Bowker enquired: Regarding the low levels of carbide formation – is that just due to higher effective oxygen level in the feed compared to usual Fischer–Tropsch (FT)?

Nico Fischer answered: This is very likely the case. The FeNi species clearly are exposed to oxidative pressure, evidenced in the partial oxidation during reaction. Furthermore, we do not see any products of CO activation, such as methane for example. It might be that the carbon deposition observed is actually taking place on the metal oxide overlayer and forms structures not conducive to incorporation into the metallic phases yielding a carbide. We know from other studies on the Mo_2C system that the carbide phase is also not maintained even though both ethane and CO_2 activation take place on the Mo_2C surface.

Joseph El-Kadi asked: In your study, good mixing of the Fe and Ni phases of the catalyst is observed, however, in other studies segregation of these phases occurs. What chemical processes are responsible for the formation of a well mixed Fe–Ni alloy in your preparation method compared with other studies?

Nico Fischer replied: We put a special focus on the synthesis of our oxidic FeNi precursors. Instead of using impregnation techniques we have employed a surfactant-free hydrothermal route which we have studied in our laboratories extensively.[1] All available characterization indicates that we retain this high degree of mixing during the reductive activation of the catalyst. What we cannot exclude is an enrichment of the bcc and fcc alloy phases with Fe and Ni respectively.

1 M. Wolf, N. Fischer and M. Claeys, Surfactant-free synthesis of monodisperse cobalt oxide nanoparticles of tunable size and oxidation state developed by factorial design, *Mater. Chem. Phys.*, 2018, **213**, 305–312.

Mikhail Sinev remarked: Oxidative dehydrogenation (ODH) with CO_2 over oxide catalysts (manganese or chromium, as in your work) is well known. On such catalysts, ethane (or another alkane) can be activated in an "elegant" way by abstraction of a single hydrogen atom, whereas on metals one can expect a much deeper activation (up to full atomization) that would lead to a range of undesirable products. What is the advantage of using metal-containing catalysts instead of bare oxides?

Nico Fischer answered: The idea of adding specific metal functionalities is to provide a second functionality that specifically supports the activation of CO_2 subsequently providing O* species to re-oxidize the surface of the oxidic material where the activation of the alkane takes place.

Graham Hutchings enquired: You have mentioned that these FeNi catalysts are active for dry reforming of methane. Dry reforming of ethane is more facile than that of methane. Can you comment on dry reforming as a competitive reaction compared with the CO_2 ODH reaction? Can you give a rough quantification of the relative amounts of dry reforming and ODH of ethane?

Nico Fischer responded: Dry reforming is certainly the main reaction CO_2-ODH is competing against thermodynamically (together with methanation of CO_2, CO and the reverse Boudouard reaction). While our catalysts seem to kinetically suppress methanation, an indication that we do not have free Ni or very Ni rich moieties present, dry reforming of ethane does take place at higher Ni contents. For the Fe_3Ni_1 and the Fe_1Ni_1 samples about 30% and 10% of the organic C in the feed end up in ethylene. The balance forms CO, in addition to the CO formed from CO_2. The observed conversion ratios of CO_2 and ethane suggest that it is not only ODH and dry reforming taking place but possibly also the reverse Boudouard with CO_2 reacting with carbon deposits also yielding CO. While not ideal ODH, the catalysts still valorize two feed molecules of low value (CO_2 and ethane) by forming a mixture of syngas and ethylene.

Moritz Wolf communicated: Can you quantify the yield of molecular H_2 from the suggested direct dehydrogenation of ethane? How much of the H_2 released is

converted *in situ* by the reduction of CO_2 *via* reverse water–gas shift (RWGS) or the reduction of oxidised surface species?

Nico Fischer communicated in reply: Unfortunately this is not possible at this stage. This has multiple reasons, first of all the mechanism of the CO_2 ODH itself. Here it is still not resolved if it is a single step reaction or a combination of direct dehydrogenation and RWGS. A recent study by the Hutchings lab suggests that even both mechanisms can occur simultaneously.[1] Secondly there is the large number of parallel reactions, such as dry reforming (producing H_2), reverse Boudouard (consuming CO_2), coking (potentially forming H_2) and methanation (consuming H_2 but not observed in the present study). Probably a number of well-designed labelling experiments are required to shed more light onto the exact pathways in the mechanism(s).

1 E. Nowicka, *et al.*, Elucidating the role of CO_2 in the soft oxidative dehydrogenation of propane over ceria-based catalysts, *ACS Catal.*, 2018, **8**(4), 3454–3468.

Simon Kondrat enquired: Can you comment on the importance of lattice oxygen in the dehydrogenation pathway on your supported chromium oxide. In particular are you inhibiting the oxygen storage capacity or perhaps more importantly the redox properties of the oxide by supporting it? Would you anticipate a change in the catalytic performance or NiFe–support interaction by changing the oxide layer thickness?

Nico Fischer responded: This is a very interesting question that we have not investigated in detail. The metal oxide overlayers we have deposited certainly differ in their properties from the bulk material. But in the present study and ongoing work, the focus was less on identifying the best bulk metal oxide support but rather to create a library of materials of varying reducibility/Lewis acidity. To translate these findings to a bulk metal oxide will require additional work.

However, it has to be said, that so far most metal oxide overlayers behave in a way we would expect from data available from their bulk counterparts.

Bert Weckhuysen asked: What about the metal alloy formation; how to further confirm what is surface *vs.* bulk of these particles? What is the exact oxidation state in these systems; and can you precisely control this?

Nico Fischer answered: This is a very challenging task. We know from offline analysis as well as from *operando* CO_2 activation studies on the materials that we do have both bulk metallic and oxidic Fe and Ni phases present in the sample. It will be near impossible to deconvolute any results from XAS, XPS, magnetometer in this context. Maybe ETEM could help with the existing systems if it is possible to identify oxidized and metallic moieties and obtain diffraction data from it. An alternative would be to develop model systems representing a pure fcc or bcc alloy, although I am not sure if the pure bcc is possible.

Bert Weckhuysen remarked: I have enjoyed listening to your talk; nice and advanced work. Regarding the use of XPS methods it is important to make sure that you are very careful how to identify oxidation state because of charging and

shifting. That certainly holds for elements such as Cr^{6+} where reduction may take place in the X-ray beam, but where also the shifts between the different oxidation states are not always that obvious. Here maybe the application of near ambient pressure might be helpful.

Nico Fischer responded: Thank you very much for the kind words. I fully agree regarding the challenges of NAP-XPS. We were fortunate enough to have beamline allocated to us in 2019 and we investigated the CO_2 activation over molybdenum carbide of which we thought it would be the easier system compared to oxide overlayer supported NiFe. Even the 'simplest' experiments proved to be challenging to evaluate due to charging and shifting effects.

Peter W. Seavill communicated: I found this to be very interesting work. Have you carried out similar studies using Fe_xNi_y catalysts on longer and more complex alkanes than ethane? If so, were there any significant differences in the results?

Nico Fischer communicated in reply: Thank you very much for the kind words. In short the answer is no, we have only looked at ethane at this stage. However, from literature and thermodynamics we expect that longer straight chains would react easier. More complex molecules, such as branched alkanes might pose a bigger challenge. One might have multiple equivalent C–H bonds that could react leading to a mixture of products.

Bert Weckhuysen opened discussion of the paper by Christian Hess: I have enjoyed listening to your talk. Have you done separate infrared experiments and do the samples allow you to do this?

Christian Hess answered: In the initial stage of the project we also performed IR experiments. However, as our particular focus was on the role of the ceria support we employed *operando* Raman spectroscopy, which at the same time provides information on the catalyst structure (*via* solid-state phonons) and the presence of surface species/adsorbates (*e.g.* peroxides, carbonates, hydroxyl groups). A comparison of the information on Au/ceria catalysts, provided by different techniques (IR, Raman, UV-Vis), has been discussed in more detail in a previous paper.[1]

1 C. Schilling and C. Hess, CO oxidation on ceria supported gold catalysts studied by combined *operando* Raman/UV-Vis and IR spectroscopy, *Top. Catal.*, 2017, **60**, 131–140.

Bert Weckhuysen asked: I was wondering if you have also performed independent IR experiments to confirm the different assignments of the Raman spectroscopy measurements? Are there any sensitivity differences between UV-Vis and vibrational spectroscopy as you are measuring them on the same sample, but probing different depths/areas/volumes of the sample? Furthermore, what is sensitivity of the two methods and how do they relate to each other?

Christian Hess replied: The assignments of the Raman bands were confirmed by $H_2^{18}O/D_2O$ isotope exchange experiments and DFT calculations, providing

a consistent and detailed picture of the observed vibrational features. Therefore, independent IR experiments were not necessary.

Operando Raman (532 nm) and UV-Vis spectra were taken in the same *in situ/operando* cell. Considering the size of the used Au/ceria particles, UV-Vis spectra provide an integral analysis. Raman spectra were collected from a much smaller area (spot size: ~15 μm) than UV-Vis spectra. Based on isotope exchange experiments we recently estimated the sampling depth of Raman spectroscopy on Au/ceria catalysts to be in the nm range.[1] Thus, regarding sampling depth, Raman spectra provide a more focused analysis of the subsurface of the catalysts.

1 C. Schilling and C. Hess, Elucidating the role of support oxygen in the water–gas shift reaction over ceria supported gold catalysts using *operando* spectroscopy, *ACS Catal.*, 2019, **9**, 1159–1171.

Richard Catlow enquired: Your proposed mechanism is particularly intriguing. Do you envisage that the CO oxidation takes place at the interface between the gold and the ceria, creating a vacancy which then diffuses away and subsequently reacts with water?

Christian Hess responded: Yes, the CO oxidation is proposed to take place at the interface, by reaction between lattice oxygen and CO adsorbed on the gold. As a result, an oxygen vacancy is created which is proposed to strongly facilitate the dissociation of water. In fact, our $H_2^{18}O$ isotope exchange experiments provide evidence for the complete dissociation of water, leading to the incorporation of ^{18}O into the ceria lattice, confirming previous more detailed isotope exchange experiments on Au/ceria catalysts.[1]

1 C. Schilling and C. Hess, Elucidating the role of support oxygen in the water–gas shift reaction over ceria supported gold catalysts using *operando* spectroscopy, *ACS Catal.*, 2019, **9**, 1159–1171.

Andrew Beale said: Regarding the properties of the Au in the Au/CeO_2 catalysts. Most of the characterisation data presented concerns the behaviour of CeO_2. However, I notice that there are some interesting changes in the UV-Vis spectra which appear to indicate evolution of the properties of the Au species. Particularly for the Au/CeO_2 nanosheet-containing sample where the greatest (comparative) change in UV-Vis spectra is seen. Is it possible then to comment on the significance of these observations and whether this has any bearing on the catalytic performance?

Christian Hess replied: When switching from Ar to reaction conditions the Au/rods show the largest changes in absorption, and the Au/cubes the smallest. The changes in absorption are related to Au plasmons and Ce^{3+}–Ce^{4+} transitions, therefore a quantitative discussion of the changes related to the Au properties is difficult based on the UV-Vis data only. The increase in absorption is related to the activity, but the absolute changes do not allow to explain the tendency in the observed WGS activities. Thus other aspects need to be considered beside ceria reducibility, as discussed in more detail in the paper (DOI: 10.1039/c9fd00133f).

Laura Torrente Murciano asked: My question is related to the gold–ceria interaction in the catalyst. It is known that size of gold and interaction of gold with ceria has effect on catalytic activity. How big are the gold particles and what is the interaction with the ceria?

Christian Hess answered: The morphology and size of the ceria particles was evaluated by using TEM, showing that neither the loading with gold nor exposure to reaction conditions induced any changes. Based on EM analysis the gold is highly dispersed, as there is no indication for the presence of larger particles. The interaction of gold with ceria was characterized by UV-Vis and XP spectroscopy, indicating the presence of both metallic and cationic gold. According to our *ex situ* XPS analysis the fraction of metallic gold ranges from 70% for Au/sheets to 40% for Au/cubes.

Laura Torrente Murciano remarked: This is an interesting piece of work. I would like to know more about the properties of the gold nanoparticles, mainly the size of the particles and their Au(0)/Au(+) ratio. Well-known papers in this field indicate that non-metallic gold is responsible for very high activities especially at low temperatures (*e.g.* ref. 1).

1 Q. Fu, H. Saltsburg and M. Flytzani-Stephanopoulos, *Science*, 2003, **301**(5635), 935–938, DOI: 10.1126/science.1085721.

Christian Hess responded: The first part of the question has been answered in the context of the previous question.

While the present work (DOI: 10.1039/c9fd00133f) focused on the role of the support properties on the mode of operation of Au/ceria catalysts, in our previous work on the CO oxidation over Au/ceria catalysts we were able to specify the state of gold under reaction conditions as single-site (pseudo single-site) cationic gold, using combined *operando* IR and DFT analysis.[1]

1 C. Schilling, M. Ziemba, C. Hess and M. V. Ganduglia-Pirovano, Identification of single-atom active sites in CO oxidation over oxide-supported Au catalysts, *J. Catal.*, 2020, **383**, 264–272.

Graham Hutchings communicated: In the discussion and in answer to the question asked by Laura Torrente Murciano you indicated that the interaction between the support and the gold nanoparticle is a very important factor in the activity of gold catalysts for the low temperature water–gas shift reaction and also for the catalyst lifetime. We have studied a different support for this reaction[1] namely ceria–zirconia; a catalyst initially highlighted by Hardacre and co-workers.[2] This catalyst is extremely active for the low temperature water–gas shift reaction, but it deactivates very rapidly. Using stop–start scanning transmission electron microscopy[1] to follow the exact same area of the sample at different stages of the LTS reaction, together with complementary X-ray photoelectron spectroscopy and we showed that agglomeration of the gold and de-wetting of the support are possible routes by which deactivation occurs. Hence using the latest microscopy techniques it is possible to investigate the interaction between the support and gold nanoparticles.

1 J. H. Carter, X. Liu, Q. He, S. Althahban, E. Nowicka, S. J. Freakley, L. Niu, D. J. Morgan, Y. Li, J. W. Niemantsverdriet, S. Golunski, C. J. Kiley and G. J. Hutchings, Activation and deactivation of gold/ceria–zirconia in the low-temperature water–gas shift reaction, *Angew. Chem., Int. Ed.*, 2017, **56**, 16037–16041.
2 D. Tibiletti, A. Amieiro-Fonseca, R. Burch, Y. Chen, J. M. Fisher, A. Goguet, C. Hardacre, P. Hu and A. Thompsett, DFT and *in situ* EXAFS investigation of gold/ceria–zirconia low-temperature water gas shift catalysts: Identification of the nature of the active form of gold, *J. Phys. Chem. B*, 2005, **109**, 22553–22559.

Christian Hess communicated in reply: Insight into the interaction between the ceria support and gold can also be provided by IR, UV-Vis, and X-ray photoelectron (XP) spectroscopy. In the presented work on the low temperature water–gas shift (LT WGS) reaction we employed mainly *ex situ* XPS and *operando* UV-Vis spectroscopy. *Operando* UV-Vis spectra show facet-dependent changes in absorption at around 570 nm, which are related to Au plasmons and Ce^{3+}–Ce^{4+} transitions. As shown in more detail in Fig. 6 of the paper (DOI: 10.1039/c9fd00133f), upon switching from reaction conditions ($CO/H_2O/Ar$) to water (H_2O/Ar) and finally inert (Ar), the absorption significantly drops but does not return to the level observed prior to reaction conditions. Consistent with the above observations for Au on ceria–zirconia, we attribute this behavior to an agglomeration of gold particles during LT WGS reaction, leading to an enrichment of neutral gold and thus an increase in plasmon absorption.

XP spectra have provided more detailed information on the state of gold in the ceria facet-dependent Au/ceria catalysts. It should be mentioned, however, that in the current *ex situ* analysis an influence of ambient cannot be excluded. In previous work on the CO oxidation over Au/ceria catalysts we have demonstrated the potential of IR spectroscopy to specify the state of gold under reaction conditions as single-site (pseudo single-site) cationic gold by using a combination of *operando* IR spectroscopy and DFT calculations.[1]

1 C. Schilling, M. Ziemba, C. Hess and M. V. Ganduglia-Pirovano, Identification of single-atom active sites in CO oxidation over oxide-supported Au catalysts, *J. Catal.*, 2020, **383**, 264–272.

Bo Yang opened discussion of the paper by Romain Réocreux: About the settings of your simulation. What parameters were changed when you take into account these absorbate–adsorbate interactions in the simulation?

Romain Réocreux replied: The only parameters that were added were the adsorbate–adsorbate interactions and their associated geometric configurations. These interactions change the probability of having two species adsorbed on neighbouring sites: the probability increases for attractive interactions or decreases for repelling interactions. This is particularly important for bimolecular elementary steps and can significantly modify the reactivity on the surface.

Bo Yang enquired: Do you need to calculate adsorption energies of surface intermediates at different coverages for the estimation of activation energies?

Romain Réocreux answered: We estimate activation energies using DFT calculations at the low coverage limit. Of course, the way adsorbates interact can modify locally the activation energies. This is accounted for *via* Brønsted–Evans–

Polanyi (BEP) relationships that estimate how much the transition state is impacted by lateral interactions based on the lateral interactions present at the reactant and product states.[1] This goes beyond the mean-field approach based on coverages, which cannot distinguish between two identical coverages associated to different adsorbate configurations or compositions.

1 J. Nielsen, M. d'Avezac, J. Hetherington and M. Stamatakis, *J. Chem. Phys.*, 2013, **139**, 224706, DOI: 10.1063/1.4840395.

Michail Stamatakis added: Just to provide a bit of background, in our kinetic Monte Carlo approach, lateral interactions are treated with the cluster expansion Hamiltonian formalism, whereby the energy of a lattice configuration is essentially decomposed into one-body, two-body and many-body contributions, which may involve short- or long-range terms. The effect of these interactions on the reaction rate constants is modelled by Brønsted–Evans–Polanyi relations. The technical details appear in our previous publication.[1] For our present paper (DOI: 10.1039/c9fd00134d), we made the assumption that only short-range interactions (first nearest-neighbour) that directly affect elementary steps are important. Thus, we did not consider, for instance, CH_2O–CH_2O lateral interactions, as there was no reaction between two CH_2O molecules.

1 J. Nielsen, M. d'Avezac, J. Hetherington and M. Stamatakis, *J. Chem. Phys.*, 2013, **139**, 224706, DOI: 10.1063/1.4840395.

Richard Catlow remarked: The role of lateral interactions is particularly interesting and has been addressed in your response to the previous question. More generally, the paper illustrates the power of the combination of DFT with kMC in unravelling reaction mechanistic details.

Christian Reece enquired: There has been some contention in places regarding kinetic Monte Carlo (kMC) *vs.* mean field microkinetic modelling, particularly when it comes to modelling lateral interactions. The problem with mean field microkinetic modelling is that we often dismiss the effect of lateral interactions at low surface coverages as we are assuming a homogeneous surface. While this may be true at high temperature, at low temperature (for example in temperature programmed reaction spectroscopy experiments) the surface coverage may be low, but there may be localised clusters of adsorbates. Do your kMC simulations show that under low surface coverage conditions there is formation of islands?

Romain Réocreux responded: In our kMC simulations, we do not observe any island formation, probably because of the low coverages considered. We also start the simulations with CH_3O* and $O*$ on the surface, so the early stages of the experiments (when methanol adsorbs on the O-precovered Au(111) surface) are disregarded. I expect that islands may form at these early stages of the experiments: $O*$ can indeed attract up to three methanol/water molecules in its first coordination shell. This can have a tremendous impact on the availability of $O*$, and potentially modulate the selectivity for methylformate *versus* CO_2.

Michail Stamatakis added: Reflecting on the issue of the choice of functional, which was discussed yesterday, it is worth noting that in the early stages of this

project we tried to use already published energetics data (obtained with PW91) in building the kMC model. However, this functional yields very strong attractive interactions between OH groups, so the kMC model was predicting stable OH clusters on surface, which did not match experimental data (OH is a highly transient species, according to experiments). However, when we started using the Tkatchenko–Scheffler van der Waals functional these interactions were correctly modelled and such clusters no longer appeared in kMC simulations.

Andrea M. Oyarzún Aravena communicated: I think kMC methods can be a useful tool to model and analyze complexes processes, where a series of reactions takes place. I would like you to make a comment about the potential of the kMC methods for modeling complex processes in a simple way.

Romain Réocreux communicated in reply: All flavours of kinetic-based analyses (energetic span model, microkinetic, kMC, …) provide useful information to identify the key elementary steps in a complex and branched reaction network. Unlike most models, on-lattice kMC simulations account for spatial correlations between adsorbates. We can describe the surface configuration of adsorbates (monodentate, bidentate, …), how two adsorbates approach each other to react (adsorption sites, orientation) and how they interact. This allows to go beyond the mean field approximations.

Christian Reece asked: As someone with an atomistic level of understanding of the surface, what experiments would you propose we perform so we can overlap and confirm whether the lateral interactions are actually important at low surface coverages and high temperatures?

Romain Réocreux replied: I am not sure how the significance of lateral interactions could be directly evidenced experimentally as, obviously, they cannot be switched on and off at will as in our kMC simulations. The comparison between the microkinetic model (mostly based on experimental data)[1] and our kMC model (purely based on DFT data) is however indirect evidence of their significance. In the microkinetic model that you have studied,[1] you have made strong assumptions regarding the role of O* in the mechanism: it is essentially limited to the activation of methanol and the formation of formate. It is never involved in the C–H cleavage steps, which, because of their bimolecularity, are the ones where lateral interactions may play an important role. When we take into account these steps in the kMC model and keep the lateral interactions switched off (scenario #3, Fig. 6 in the paper; DOI: 10.1039/c9fd00134d), the simulated temperature programmed desorption (TPD) spectra do not agree very well with experimental data, essentially because O* is too reactive in C–H activation steps. When the lateral interactions are switched on (essentially repelling for the C–H activation steps), there is better agreement with experimental data. Surprisingly we can achieve similar agreement (at least for the temperature peaks) with models that do not include the O* mediated C–H activation steps. This suggests that the strong assumptions, limiting the role of O* to $CH_3OH^* + O^* \rightarrow CH_3O^* + OH^*$ and $CH_2O^* + O^* \rightarrow CH_2O_2^* \rightarrow HCOO^* + H^*$ in the microkinetic model,

hold precisely because of the lateral interactions, which penalise O* mediated C–H activation steps. A closer look at scenario #2 (Fig. 5 in the paper) (where O* mediated C–H activation is neglected) indeed shows that lateral interactions do not affect too much the position of the peaks but they greatly change the $HCOOCH_3 : CO_2$ selectivity.

1 C. Reece and R. J. Madix, *ACS Catal.*, 2021, **11**, 3048–3066.

Mikhail Sinev requested: Could you please comment on the properties of O-species on gold: how strongly they are bound to the surface? Does the binding energy depend on coverage?

Romain Réocreux answered: O adatoms (referred to as O*) are generated upon ozone exposure ($O_{3(gas)} \rightarrow 3O*$) on Au(111) surfaces under ultra-high vacuum conditions. Once generated, O* can associatively desorb as $O_{2(gas)}$ at around 500–600 K.[1] Thus, O* is kinetically stable in the range of temperatures considered in our simulations. The lateral interaction between two O* adsorbed on neighbouring fcc sites is 0.28 eV: the binding energy of O* is expected to be coverage dependent. In our simulations we only considered a very small amount of O* (0.02%) and therefore did not include this lateral interaction.

1 D. Holmes Parker and B. E. Koel, *J. Vac. Sci. Technol.*, 1990, **8**, 2585.

Mikhail Sinev enquired: According to the standard thermodynamics of the "gold–oxygen" system, the dissociative adsorption of di-oxygen is endothermic, and, correspondingly, recombinative desorption should be exothermic and highly probable. Do you consider desorption of oxygen in your study?

Romain Réocreux replied: As mentioned in my previous response, the associative desorption of O* as $O_{2(gas)}$ is extremely activated and only happens for temperatures above 500 K. The desorption of $O_{2(gas)}$ was therefore not included in our model.

Mikhail Sinev questioned: Do you consider desorption of oxygen in your study? How fast is it compared to the reaction with methanol?

Romain Réocreux responded: Unlike the associative desorption of O* as $O_{2(gas)}$, the acid/base reaction of O* with CH_3OH* ($O* + CH_3OH* \rightarrow OH* + CH_3O*$) is only slightly activated (activation energy of 0.26 eV). It is a fast reaction that can happen at very low temperatures.

Michail Stamatakis added: The O_2 dissociative adsorption energy calculated *via* the PBE-TS functional is negative indicating exothermic adsorption ($O_{2(gas)} \rightarrow 2O*$; $\Delta E_{rxn} = -0.73$ eV). There are, however, severe kinetic limitations in the dissociation of oxygen on Au, and this is why, in the surface science experiments, O_3 (ozone) was used to get O* adatoms on the surface. In reactor experiments, nanoporous gold was used, which has a small amount of Ag atoms in the surface that facilitate O_2 dissociation.

Mikhail Sinev asked: What is the H-affinity (in energy terms) of surface oxygens? What is the way they activate the methanol molecule?

Romain Réocreux answered: Methanol molecules are activated by a surface acid–base reaction with O* adatoms yielding surface OH and methoxy. Methanol and O* interact *via* a hydrogen bond (interaction energy of −0.24 eV).

Philip Davies enquired: Does your model take into account the possibility of adsorbate islanding? Methoxy for example forms islands on Cu(110) and this affects the kinetics of the oxidation reaction.[1]

1 P. R. Davies and G. G. Mariotti, *Catal. Lett.*, 1997, **46**, 133–135.

Romain Réocreux replied: In principle our model does take into account the possibility of adsorbate islanding as we have included lateral interactions. However, since we have limited the description of the lateral interactions to the first nearest neighbours, the energetics of such hypothetical islands would not be highly accurate. This is not really a problem in our work as the coverages are very low. Regarding methoxy on Au(111) more specifically, our calculations suggest that two methoxy adsorbed on neighbouring sites tend to repel each other (interaction energy of 0.15 eV). Longer range interactions would need to be computed to completely rule out the formation of methoxy islands on Au(111) surfaces.

Keith Whiston opened a general discussion: Determination and quantification of gold oxidation states. What else needs to be done in the area of advanced analytical techniques to improve the determination and quantification of gold oxidation states? What are the outstanding pitfalls?

Christian Hess responded: As mentioned in the above discussion, in our previous work on the CO oxidation over Au/ceria catalysts we have demonstrated the potential of IR,[1] and in particular combined IR and DFT analysis[2] to specify the state of gold, even under reaction conditions. In this context, careful analysis is required (*e.g.* performing isotope exchange experiments) due to the possible presence of a Ce^{3+}-related electronic transition.

1 C. Schilling and C. Hess, CO oxidation on ceria supported gold catalysts studied by combined *operando* Raman/UV-Vis and IR spectroscopy, *Top. Catal.*, 2017, **60**, 131–140.
2 C. Schilling, M. Ziemba, C. Hess and M. V. Ganduglia-Pirovano, Identification of single-atom active sites in CO oxidation over oxide-supported Au catalysts, *J. Catal.*, 2020, **383**, 264–272.

Nico Fischer answered: We have no experience working with gold, so I cannot really answer this specific question.

Graham Hutchings noted: Keith asks a very interesting point concerning how can the oxidation state of gold be determined in active catalysts. For supported gold nanoparticles the main technique is X-ray photoelectron spectroscopy which is an averaging technique. An added difficulty is that many catalysts have very low concentration of gold (<1%) and this adds to the sensitivity issues. In addition,

cationic gold can be readily reduced to metallic gold under vacuum in the XPS measurement as I noted in my opening talk (DOI: 10.1039/d1fd00023c) for this discussion. It would be interesting to hear whether there are now improved ways to investigate supported gold nanoparticles.

Nico Fischer commented: The problem of identifying the oxidation state of low concentration gold in a catalyst is very much the same experienced for any metal nanoparticle. While for gold the actual Au concentration might be low, for less noble nanoparticles, the concentration of surface sites or interface sites which might be active for the respective reaction is equally low. Even surface sensitive techniques still struggle to provide accurate insights on oxidation states of minority surface species, both regarding speciation and localization. While the community should continue to develop technologies and methods to get closer to the necessary resolution, we should not forget that reliable correlations between bulk structures and activity are very valuable. We might not know exactly the nature of the active phase, but we might be able to provide a description of the bulk structure on which the active phase forms reproducibly.

Graham Hutchings added: I agree that the problems of trying to investigate supported nanoparticles are not unique to gold. Gold does have the additional problem in that cationic gold is readily reduced and many characterisation techniques can induce this reduction and so the presence of cationic gold can be missed. Perhaps *in situ* spectroscopies using probe molecules might add some progress.

Graham Hutchings noted: We are more fortunate for catalysts which have well dispersed gold cations as now EXAFS and XANES can be used and the XANES white line height is indicative of the oxidation state of gold.[1] With care XPS then can be useful too. But as soon as you have a range of structures present then this is a problem, as you are averaging across a lot of structures. There are many supported single cation catalysts now – not just gold.[2] When nanoparticles are present together with clusters and cations, most atoms are within the nanoparticle, and in this case the nanoparticle might not be active at all. For supported gold palladium nanoalloys the oxidation state of gold is typically Au^0 but often Pd can be oxidised but this depends on the nature of the oxidising/reducing nature of the environment and this can lead to core–shell structures being formed.[2]

1 G. Malta, S. A. Kondrat, S. J. Freakley, C. J. Davies, L. Lu, S. Dawson, A. Thetford, E. K. Gibson, D. J. Morgan, W. Jones, P. P. Wells, P. Johnston, C. R. A. Catlow, C. J. Kiely and G. J. Hutchings, Identification of single-site gold catalysts in acetylene hydrochlorination, *Science*, 2017, **355**, 1399–1402.
2 X. Sun, S. R. Dawson, T. E. Parmentier, G. Malta, T. E. Davies, Q. He, L. Liu, D. J. Morgan, N. Carthy, P. Johnston, S. A. Kondrat, S. J. Freakley, C. J. Kiely and G. J. Hutchings, Facile synthesis of precious-metal single-site catalysts using organic solvents, *Nat. Chem.*, 2020, **12**, 560–567.

Andrew Beale remarked: I would generally agree that the interrogation of the oxidation state in terms of the appearance/absence of particular features in the XANES is generally more tractable for Au species than for most of the catalytically interesting elements. Differences in molecular orbital energies/density of states when the coordinating ligand type (*e.g.* C *vs.* O) changes and maybe even the

particle size/shape will also affect XANES feature intensities rendering this less reliable however. *A priori* knowledge of the catalyst/catalytic system is therefore important when extracting oxidation state information using XANES.

Dmitry Eremin said: Gold indeed prefers to stay as gold(0), but is it possible to assume, that for Pd/Au alloys or even single atom systems interfacial phenomena and synergistic behavior of the Au–Pd pair can benefit both metals? Palladium in Pd(0) heterogeneous catalysts nearly always has Pd(II) impurity by XPS measurements. Can these metals control the electron flux and Pd will remain Pd(0), while Au will remain as Au(I)?

Graham Hutchings responded: With respect to Pd nanoparticles the interaction with the support and the gas phase are important and the oxidation state of the surface of the nanoparticle depends on oxidising ability of gases/phases above it/the surroundings. In a reducing environment, the surface prefers to be metallic Pd(0). In an oxidising environment the surface prefers to be Pd(II). This is not observed with gold nanoparticles.

Dmitry Eremin opened discussion of the paper by Bert Weckhuysen: How precisely can the conversion be followed? Is it possible to attach a drive and synchronise the motion with the flow, so that camera with high resolution follows the same particle while it is going through the channel?

Bert Weckhuysen replied: That is possible and AI should also make it possible to do that in a more automated manner. Regarding the precision, that is fairly high, especially at the first stages of the decoloration reaction, as then the colour differences are high enough to be picked up by the camera/detector. Statistics-wise I cannot put a number on it as we did not work it out as such.

Dmitry Eremin asked: If trying to apply SERS for single particle diagnostics, should only Au or Ag nanoparticles be used? Or can Pd be applied as well, as it might also cause surface plasmon resonance.

Bert Weckhuysen responded: In that case you have to make use of Au or Ag nanoparticles as that is required for having sufficient SERS signal enhancement. Another approach is to make use of inline SERS-active substrates.

Nico Fischer enquired: Do you see a possibility to extend this approach from a single droplet–single catalyst particle to a single droplet with various catalyst particles which are kept under constant mixing in the droplet due to vortex effects *etc.*? This would potentially allow for slightly different questions to be asked, for example a varying mixture of liquid reactants, which is set at the inlet point of the microreactor.

Bert Weckhuysen answered: This is a very interesting comment/suggestion, which is worthwhile to study further. Actually what we notice is that we sometimes have two or three particles in one droplet, but that is rather accidental. What would be nice is now to do this in a controlled manner; this requires some further thinking but should be possible to perform, providing we can have indeed

a very good mixing in the droplet due to vortex effects. An idea is to do first the mixture and inject that and hope for more than one particle per droplet; another one is to add later on in the micro-reactor system the second particle in the droplet; and make the droplet a bit larger. Many thanks for this very good idea, although we have to see how to realise this in practice.

Laura Torrente Murciano asked: This is a very elegant example of a three phases system in flow. One of the main issues in this type of reaction is the low solubility of hydrogen in solvents. As an engineer, I have an interest in mass transfer limitations in these system. Your paper (DOI: 10.1039/d0fd00006j) states that the system is not mass transfer limited, but do you have any evidence? You state that the diffusion in ethanol is quite high but saturation level might be low and your reaction is very fast (completed in 8 seconds) – do you have any evidence that you are not mass-transfer limited?

Bert Weckhuysen replied: I agree with you that this is an issue; and as we have indicated in the paper (DOI: 10.1039/d0fd00006j) we have been evaluating the diffusion of H_2 in the different solvents used. We cannot be sure that mass transfer limitation is not an issue, but the PDMS membrane will not be the issue; the issue could arise in the droplet when in contact with the catalyst particle and now knowing very well the hydrodynamics of the liquid–gas surrounding the catalyst particle. Hence, we cannot rule out that there is no mass-transfer, although my gut feeling tells that I am not sure about this.

Laura Torrente Murciano queried: Following the previous question, have you tried to increase the pressure of hydrogen or modify the concentration of reactants?

Bert Weckhuysen answered: We have changed the hydrogen concentrations but not the pressure. It is relatively easy to change the ratio of reactants and also add different amounts of hydrogen. Hence, various reaction conditions could be studied with the microreactor technology developed in this work.

Laura Torrente Murciano asked: And if you stop the flow, do you observe the same level of conversion? I am asking this because under bi-phasic flow, you are expecting rotation vortices inside the droplets which in this case, will enhance mass transfer within them.

Bert Weckhuysen responded: This is a clever comment; and worth further studying. What we observe is that when the flow is stopped we can take snapshots and follow the conversion as function of time for each of the droplets. This was used to develop the calibration lines on the decoloration reaction taking place as a result of the hydrogenation of the dye molecule.

Froze Jameel requested: Could you comment on the solubility of hydrogen in other solvents such as methanol?

Bert Weckhuysen answered: I do not know this by heart, but believe that different solvents would be suitable to perform this droplet reactor approach.

Moritz Wolf enquired: (Stabilised) nanoparticles from separate syntheses, such as colloidal methods, can be easily dispersed in various solvents using ultrasonication and may already display catalytic activity. Can you study the catalytic activity of such dispersions of nanoparticles as well? This would not correspond to single particle diagnostics any more as one would analyse the integral catalytic performance of numerous nanoparticles, but the absence of a support lowers the density drastically enabling great control over the desired flows.

Bert Weckhuysen responded: I do not believe that it is limited to the systems we have described in this work. It can be indeed be expanded to other synthesis routes, such as colloidal approaches. Numerous particles can be also studied; the aim was here to make a platform to study single catalyst particles, but certainly this is an interesting avenue worth to further explore.

Moritz Wolf asked: How do you assess the possibility to invert the application of the cell to study catalytic three-phase reactions with liquid reactants and gaseous products, *i.e.* with a gas phase evolving alongside the reaction progress? An interesting example would be the catalytic dehydrogenation of liquid hydrocarbons.

Bert Weckhuysen replied: I agree that this would be a very nice approach to elucidate and you made me think about this. One of the issues, which we have to handle directly will be to make sure that you perform this at higher temperatures as dehydrogenation catalysis requires a higher temperature than hydrogenation catalysis. In any case, I am convinced that reactor design can be altered to accommodate a gas–liquid–solid reaction at elevated temperatures and pressures.

Andrew Beale said: You're getting lots of data with this method which is really powerful, could even be used to drive optimisation of reactions provided the large volumes of data generated can be harnessed. Fig. 6 in the paper (DOI: 10.1039/d0fd00006j) shows the particles to contain various shades of brown and blue and perhaps on closer inspection even some radial gradient/variation so I wondered whether you can extract more information on the distribution of 'colour'/maybe even chemical speciation from the photographs to obtain deeper information which may be necessary for reaction optimisation?

Bert Weckhuysen replied: Many thanks for the interesting and valuable question, Andy. It is indeed so that a lot of data are obtained; and also that many particles can be investigated and captured with the method we have now developed. There are two approaches one now can follow; either you take the UV-Vis microscope; or you take a high-end camera with a macro-lens which allows you to focus on the large variety of the particles. Both approaches allow to assess the intra-particle heterogeneities (spatial differences within one catalyst particle) and inter-particle heterogeneities (differences between the different catalyst particles). As within life-sciences, what you wish is to see which particle is "healthy" or working very well; and which particle is "less healthy" or performing less well. This is now possible; and you can even based on this method separate them and analyse them afterwards. Important to realise is however that this requires the

analysis of a large dataset, which you cannot do any more manually, but have to do this with data mining routines. We have in our group a very talented senior researcher, Associate Professor Florian Meirer, who writes his own programs to make this possible. In this way, large data sets can be analysed in an objective and systematic manner. Colours should hence be analysed in terms of an objective parameter; in our work we have put RGB value; and found that the red value is the one which goes hand in hand with the decoloration reaction during this hydrogenation catalysis.

Ali Reza Kamali opened discussion of the paper by Justin Hargreaves: Thank you Professor Hargreaves for presenting this interesting work! I am wondering what was the lithium precursor and the method used for the Li doping. I am also curious to know whether the doped material has been characterised to detect any influence that lithium might have on the structure of the manganese nitride. Can you comment on these please?

Justin Hargreaves responded: Thank you very much indeed for your question. The precursor oxide was prepared by co-precipitating lithium hydroxide hydrate and manganese nitrate using ammonia as a precipitating agent at pH 11 and 50 °C. The precipitate was then calcined under static air at 800 °C for 8 hours resulting in the formation of $LiMn_2O_4$ and LiO_2. The nitride phase was obtained by the reaction with sodium amide in a sealed autoclave filled with argon at 240 °C for 36 h. The resultant material was then washed with ethanol and then water prior to drying overnight. Our diffraction based studies do not indicate any structural modification associated with the presence of the lithium promoter.

Christian Hess asked: The question is related to the preparation and characterization of the Li containing catalyst. What is the location of the Li after calcination? What is the influence of the amount of Li dopant on the catalytic performance?

Justin Hargreaves answered: Many thanks for your question. Powder X-ray diffraction studies undertaken on the calcined precursor prior to nitridation indicate the presence of LiO_2 and $LiMn_2O_4$. After nitridation, no distinct lithium containing phase was evident. Currently we do not have any data relating the material's performance to systematic variation of lithium content.

Laura Torrente Murciano enquired: Many thanks for this interesting work, Justin. Related to the previous question, where is the Li? Is it close to or under the surface? Is it possible that the incorporation of Li into the crystal structure leads to a localised distortion of the structure?

Justin Hargreaves replied: Thank you very much for your question. Currently, within the limits of our measurements, which are essentially diffraction based, we do not have any definitive answer for the location of the lithium component. It is possible that it is in a near surface region where it could have a local structural distortional effect.

Constantinos Zeinalipour-Yazdi added: As a co-author of the manuscript that is under discussion (DOI: 10.1039/c9fd00131j), I would like to make a comment based on an earlier question about whether Li enters the lattice of η-manganese nitride. From the calculations, Li didn't seem to enter at the intrinsic nitrogen vacancy sites as the barrier for Li entry was high. It would be nice though to explore such possibility with experimental techniques.

Graham Hutchings asked: How mobile is the lithium in your catalyst, is there loss of lithium on use and does it lead to sintering of the catalyst? By analogy with the effect of alkali dopants on oxidative methane coupling similar catalytic effects could be observed if lithium is replaced by higher alkali metal cations (Na^+, *etc.*) if the concentration was decreased. Can you observe similar effects? If lithium is unique is there a structural hypothesis for why this is the case?

Justin Hargreaves responded: Thank you very much for your question. The lithium is very mobile and we find there to be loss at each step – material synthesis, application and the limited studies which we have applied to date in terms of regeneration. Our surface area measurements do indicate that lithium is associated with the loss of surface area. Although we have not systematically varied its concentration, we have undertaken investigations applying potassium as a promoter.[1] The behaviour is markedly different and it is clear that lithium has a uniquely beneficial role in this context – as to why this is, it is difficult to say currently on the basis of the measurements we have made, although its small size and potentially more polarising nature are factors to bear in mind.

1 S. Laassiri, C. D. Zeinalipour-Yazdi, C. R. A. Catlow and J. S. J. Hargreaves, *Appl. Catal., B*, 2018, **223**, 60–66.

Mzamo Shozi communicated: Did you try looking at the other earlier alkali metals (*i.e.* K or Na) as dopants?

Justin Hargreaves communicated in reply: Thank you for your question. We investigated potassium. It did not produce the same significant effect that we observe in the case of lithium.

Laura Torrente Murciano questioned: You mention in your paper the Mars–van Krevelen mechanism, is it right to make similarities between an oxidation reaction taking place on a ceria-based catalyst where O_2 gets incorporated into the ceria structure and this case for N_2? Is this the correct way of understanding it?

Justin Hargreaves answered: Thank you very much for your question. As detailed elsewhere,[1] we have been interested in the possibility of nitrides catalysing ammonia synthesis *via* a Mars–van Krevelen mechanism. This is the origin of our current study. It would be a nitrogen analogue of the oxidation pathway you mention.

1 C. D. Zeinalipour-Yazdi, J. S. J. Hargreaves, S. Laassiri and C. R. A. Catlow, *Phys. Chem. Chem. Phys.*, 2018, **20**, 21803–21808, DOI: 10.1039/c8cp04216k.

Collin Smith enquired: You mention in the paper (DOI: 10.1039/c9fd00131j) the selectivity is an issue for these nitride materials – what is the selectivity? In particular, is any molecular nitrogen produced during reduction?

Justin Hargreaves responded: Thank you very much indeed for your question. At close to complete denitridation of the material at 400 °C, it is our observation that the selectivity of the lattice nitrogen converted to ammonia is close to 16%. We anticipate that the remaining nitrogen lost is in the form of dinitrogen.

Collin Smith asked: You mention equilibrium is now different compared to typical ammonia catalysis – what is the new equilibrium? In particular, if in a closed cylinder with atmospheric hydrogen, what would the final (approximate) pressures of hydrogen and ammonia be?

Justin Hargreaves replied: Thank you for your question. The looping approach might be a method for generation of ammonia at ambient pressure which could have niche applications, but our interest has been centred upon the more fundamental materials chemistry related aspects of the manganese nitride based system. I do not have access to appropriate thermodynamic data in relation to your question.

Nico Fischer enquired: Is the total amount of N/NH_3 released from this system enough for a technical application or is the mass of the Mn "carrier" too high?

Justin Hargreaves responded: Thank you for your question. Our studies have been more fundamental in nature rather than centred upon application. It may be that there could be niche applications for such materials. At 400 °C the proportion of lattice nitrogen converted to ammonia over 5 hours is close to 16% in our measurements.

Nico Fischer commented: It would be very interesting to conduct a rough economic feasibility to understand the potential market for such a technology. Maybe in the area of decentralized green H_2 storage it could play an important role.

Justin Hargreaves replied: Thank you very much for your comment.

Laura Torrente Murciano asked: Would it be possible to use these materials as standard Haber–Bosch catalysts rather than in chemical looping or does one need different conditions to release and activate N?

Justin Hargreaves answered: Many thanks for your question. We were interested in applying the materials as more conventional catalysts but in our experience they do not operate catalytically and the lattice nitrogen was lost under our testing regimes.

Mikhail Sinev remarked: If we compare the data on the formation of ammonia upon addition of hydrogen and the data on the isotopic exchange of nitrogen,

then it is more likely that lithium affects the binding energy of nitrogen in the lattice than in any way participates in the activation of hydrogen.

Justin Hargreaves responded: Thank you very much for your comment. I would certainly agree that there is a very evident and pronounced effect of the presence of lithium on the loss of lattice nitrogen.

Mikhail Sinev enquired: Could you please comment on the lattice nitrogen binding energy in undoped and Li-doped materials? Have you applied any experimental methods to measure it, similar to the *in situ* calorimetry that we used to study the properties of lattice oxygen in OCM and ODH oxide catalysts?

Justin Hargreaves answered: Many thanks for your question. Our measurements certainly indicate that lithium doping enhances the loss of lattice nitrogen implying that it is more weakly held. We have not directly measured the binding energy and this would be a point of definite interest for us.

Keith Whiston asked: What happens to the bulk solid state properties of the material *e.g.* surface area, during and after use, do they change? In particular is there a significant change, I assume reduction, in BET SSA after experimental use?

Justin Hargreaves answered: Many thanks for your question. The BET surface area prior to reaction was determined to be 11 m^2 g^{-1}. We do not have a value for the post-reaction material. It has been our experience that following denitridation materials can be prone to oxidation upon discharge from the microreactor and so we would be concerned about the representative nature of such values.

Keith Whiston questioned: What is the bulk density of the manganese nitride and does the lithium doping impact that? I assume that it is a dense material?

Justin Hargreaves answered: Thank you very much for your question. I do not have a precise bulk density value, but the materials we have studied do possess reasonable surface areas.

Keith Whiston added: Conceptually I would imagine that there should be a significant change in the solid state properties of the material due to the significant N migration within the nitrides.

Diyuan Li opened discussion of the paper by Mercedes Boronat: I am curious about the mechanism outlined with a red box in Scheme 2 in the paper (DOI: 10.1039/c9fd00126c), for non-noble metals. Is the second intermediate in a nitrene form? According to my previous study and literature precedent (*e.g.* ref. 1), arene nitrene (PhN) could do ring expansion to give a seven membered ring product. During your study, has any seven membered ring product been detected?

1 V. Voskresenska, R. M. Wilson, M. Panov, A. N. Tarnovsky, J. A. Krause, S. Vyas, A. H. Winter and C. M. Hadad, *J. Am. Chem. Soc.*, 2009, **131**, 11535–11547.

Mercedes Boronat replied: The second intermediate in Scheme 2 (DOI: 10.1039/c9fd00126c) could not be strictly considered a nitrene because it is strongly bonded to the metal surface through three N–Ni, N–Co or N–Cu bonds. That is, its electronic structure does not match that of a nitrene because it doesn't have four non-bonded electrons in the valence shell. Nevertheless, we should consider the reactivity you suggest and explore the possibility of ring expansion to give a seven membered ring product. If this possibility is hindered by the three strong N–metal bonds present in the intermediate, we will obtain high activation energies and then will discard it. Regarding the detection of seven membered ring products, this is a theoretical study and we hadn't considered this possibility. But we are working on the experimental confirmation of the proposed mechanisms by IR spectroscopy using Ni/SiO$_2$, Cu/SiO$_2$ and bimetallic MCu/SiO$_2$ catalysts. If we find theoretically that ring expansion of the second intermediate is energetically accessible, we will try to confirm it experimentally.

Megha Anand asked: Nitrobenzene does not adsorb in parallel fashion on copper. Why is it so? What kind of substituents can be added to the benzene ring in nitrobenzene to make it adsorb in a flat manner on copper?

Mercedes Boronat responded: Nitrobenzene does not adsorb parallel on copper because the d-band of copper is filled and there is a repulsive interaction with the π electrons of the aromatic ring. Copper interacts with the oxygen atoms of the nitro group and this is why the molecule is normal to the surface, interacting only through the nitro group.

Philip Davies questioned: In your work you estimated the adsorption energy of nitrogen at the surface (Fig. 11 in the paper (DOI: 10.1039/c9fd00126c)). Did you allow for the reconstruction of the substrate in those calculations?

Mercedes Boronat replied: Yes, we always allow for a partial reconstruction of the substrate. In all calculations the metal catalyst is simulated by a supercell slab model containing five atomic layers oriented along the (111) plane. The two uppermost layers are always allowed to relax without restrictions, but the metal atoms in the three bottom layers are kept fixed in their bulk optimized positions. This means that we allow for the reconstruction of the catalyst surface, but not for a complete reconstruction of the whole system.

Philip Davies enquired: Do you think atomic steps at the surface would have a big impact on your conclusions?

Mercedes Boronat answered: No, not a big impact. I think that the differences between noble and non-noble metals due to their different electronic structure are so large that the main trends and conclusions would not change if we considered stepped surfaces instead of the perfect (111) surface. Of course, the presence of defects like steps could change the relative stability of some intermediates, and would probably facilitate the activation of H$_2$ in the case of Cu. But the strong affinity of non-noble metals to form M–O bonds thus enhancing the direct dissociation of the N–O bonds leading to a different reaction mechanism as

compared to noble metals is a clear conclusion which I don't expect to change with the inclusion of steps

Jennifer Edwards asked: It's clear there is potentially a very beneficial effect of CuNi alloyed catalyst for this reaction. Are you collaborating with experimentalists to synthesise these materials? What would your ideal catalyst look like (in terms of NiCu composition, random alloy, bimetallic, core–shell nanoparticles)? Have you progressed with mechanistic validation with these catalysts?

Mercedes Boronat answered: Yes, most researchers working at ITQ are experimentalists, and we are collaborating with Dr Patricia Concepción in the preparation and spectroscopic characterization of these bimetallic systems. The ideal catalyst should have isolated Ni atoms at the Cu surface, because just one Ni atom is able to dissociate H_2 but not to adsorb the reactants parallel to the surface. In principle, according to theory, there is not a critical particle size nor a preferred distribution of the two metals except that the amount of Ni should be low in order to have it highly dispersed. At present we are synthesizing relatively large metal particles supported on SiO_2 and following the reaction by IR spectroscopy to identify the intermediates and detect if there is catalyst restructuration. In the case of Ni we observe the formation of nitroso intermediate (Ph–NO) from nitrobenzene (Ph–NO$_2$), which confirms the proposed mechanism. In the case of Cu we don't observe reaction, and in the case of NiCu it depends on the amount of Ni, too little Ni remains in the bulk and it behaves like Cu. Catalyst composition must be still optimized, and also the possibility of restructuration by interaction with reactants and products must be investigated.

Patrick Morgan opened discussion of the paper by David Lennon: What effect might you expect from the speciation of the copper salt? If you changed from $CuCl_2$ to $CuBr_2$ or CuF_2, or some other salt, would you expect the analogous acid, or is this reaction specific to $CuCl_2$?

David Lennon answered: This is an interesting question. The short answer is "I don't know". The Cu(II)Cl$_2$ catalyst is matched to produce COCl$_2$, with the catalyst intended to be the source of the chlorine (eqn (8) in the paper; DOI: 10.1039/d0fd00014k). So, by analogy, it could be possible to use $CuBr_2$ or CuF_2 to access, respectively, $COBr_2$ and COF_2. However, as illustrated in the paper, in the absence of a chlorine pre-treatment and at ambient pressure, eqn (8) is inactive. Therefore, it is thought unlikely that the equivalent bromination and fluorination reactions would be practical to any reasonable degree in an ambient pressure flow system. However, Weber and co-workers describe a sequential batch procedure that involves phosgene formation over a CuCl$_2$ catalyst at elevated pressure.[1] Therefore, trial experiments employing a batch reactor operating at elevated pressures of CO over $CuBr_2$ or CuF_2 may be worthwhile exploring. That said, the hazardous nature of such experiments must be acknowledged.

1 T. Zhang, C. Troll, B. Rieger, J. Kintrup, O. F.-K. Schlüter and R. Weber, *J. Catal.*, 2010, **270**, 76.

Graham Hutchings asked: Does the chlorine added in the pretreatment step map onto the amount of phosgene made? On long term use does CO_2 formation start again?

David Lennon replied: A pragmatic question concerning process viability. No, the phosgene return is a fraction of the chlorine expended in the pre-treatment process. For example, with reference to the paper (DOI: 10.1039/d0fd00014k), Fig. 13 presents the maximum $COCl_2$ flow rates as a function of the extent of the chlorine pre-treatment. A chlorine exposure of 32.3 mmol Cl_2 $g_{(cat)}^{-1}$ induces a maximum phosgene flow rate of only 0.013 mmol $COCl_2$ $g_{(cat)}^{-1}$, *i.e.* 0.04% of the incident chlorine flux. Furthermore, as indicated in Fig. 14, the induced phosgene formation then progressively decreases as a function of time. Under the stated reaction conditions, this constitutes uneconomic chemistry!

Fig. 16a(iii) considers the case when a chlorine pre-treated catalyst has been left isolated in an inert atmosphere for 12 h then re-exposed to a continuous stream of CO at 653 K. Interestingly, a distinct increase in the maximum flow rate of CO_2 is observed. With reference to the paper under discussion (DOI: 10.1039/d0fd00014k), the chlorine pre-treatment is thought to depopulate hydroxyl groups at the $CuCl_2$/support interface that would otherwise facilitate CO oxidation *via* eqn (12). It is tentatively suggested that the re-emergence of the CO_2 signal in these experiments reflects the diffusion of hydroxyl groups from within the network of the support material to the active sites, that then facilitates the CO oxidation stage. Although only performed once, the 12 h passivation period implies that the diffusion of hydroxyl groups from the bulk to the surface region is a slow process.

Simon Kondrat remarked: The role of chlorine pre-treatment on creating specific surface species could be investigated by detailed XPS of the Cl 2P region and also by Cl K-edge XANES. The XANES can be informative on Cl speciation where metal–chloride bonds, "inorganic" chloride anions and covalently bonded chlorine can be easily differentiated.[1] Further, the Cu–Cl bond shows up as a clear pre-edge feature in which bridged and terminal Cu–Cl bonds are determinable.[2] I think that *in situ* XPS/XAFS would be very helpful in identifying reactive Cl species. *Ex situ* Cl XANES of samples dried and pre-treated might also be informative.

1 G. Malta, *et al.*, *Chem. Sci.*, 2020, **11**, 7040, DOI: 10.1039/d0sc02152k.
2 T. Glaser, B. Hedman, K. O. Hodgson and E. I. Solomon, *Acc. Chem. Res.*, 2000, **33**, 859, DOI: 10.1021/ar990125c.

David Lennon responded: I agree. This is all correct. However, to a degree, the application of these high-level analytical techniques is compromised by the hazardous nature of the reaction system. Most of our experiments had to be performed within a defined laboratory facility; measurements external to the facility were invariably limited in scope. We did explore the possibility of undertaking Cl K-edge XANES at a suitable facility, but we encountered problems within the safety assessment process. Nonetheless, we have undertaken a series of XPS and copper K-edge XAFS measurements in connection with this reaction system. Fig. 12 of the paper under consideration (DOI: 10.1039/d0fd00014k) presents Cu(2p) XPS spectra of the $CuCl_2$/KCl/attapulgite catalyst on progressive

warming, and then on exposure to CO. Those measurements provide information on the reduction of Cu^{2+} to Cu^+ by CO. A series of XANES and EXAFS measurements of the catalyst have been reported in an earlier *Faraday Discussions* article.[1] For example, the XANES measurements establish that at the elevated temperatures connected with phosgene formation the catalyst is comprised of Cu^+ and a small amount of Cu^{2+}. DFT calculations indicate that a mixed Cu^+/Cu^{2+} catalyst is required to support CO chemisorption.[1]

1 S Guan, P. R. Davies, E. K. Gibson, D. Lennon, G. E. Rossi, J. M. Winfield, J. Callison, P. P. Wells and D. J. Willock, *Faraday Discuss.*, 2018, **208**, 67–85, DOI: 10.1039/c8fd00005k.

Keith Whiston asked: Superficially this is a fairly simple catalyst, but do you have any comments or observations about the support. Is there anything special about the clay which is used?

David Lennon answered: A central concept in the design of the catalyst is that it is must be durable to the harshness of the corrosive oxy-chlorination conditions. In fact, the $CuCl_2$/KCl/attapulgite catalyst under consideration is an industrial grade oxychlorination catalyst that finds application in the manufacture of the refrigerant feedstocks trichloroethene and tetrachloroethene *via* the oxychlorination of dichloroethane.[1,2] Attapulgite is the mineralogical name for palygorskite, a porous material formed from interspersed sheets of silica and sheets of octahedrally co-ordinated cations drawn from Mg^{2+}, Al^{3+} and Fe^{3+}.[3] One of the reasons for its selection as a support material is due to favourable abrasion resistance in large-scale fluidised bed operation.

With reference to the paper under discussion, the IR spectrum of the dried catalyst (Fig. 4) shows the presence of hydroxyl groups and water molecules within the structural framework, which are thought to be located in the galleries of this clay like material.[4] As indicated schematically in Fig. 17, hydroxyl groups present at the $Cu(\text{II})Cl_2$/support interface are thought to be responsible for the CO oxidation pathway (eqn (12)).[4]

1 I. W. Sutherland, N. G. Hamilton, C. C. Dudman, P. Jones, D. Lennon and J. M. Winfield, *Appl. Catal., A*, 2011, **399**, 1–11.
2 I. W. Sutherland, N. G. Hamilton, C. C. Dudman, P. Jones, D. Lennon and J. M. Winfield, *Appl. Catal., A*, 2014, **471**, 149–156.
3 S. Guan, P. R. Davies, E. K. Gibson, D. Lennon, G. E. Rossi, J. M. Winfield, J. Callison, P. P. Wells and D. J. Willock, *Faraday Discuss.*, 2018, **208**, 67–85.
4 S. Guan, G. E. Rossi, J. M. Winfield, C. Wilson, D. MacLaren, D. J. Morgan, P. R. Davies, D. J. Willock and D. Lennon, *Faraday Discuss.*, DOI: 10.1039/d0fd00014k.

Keith Whiston enquired: Do you have any general comments about how the catalyst could be improved? Or do you think it represents the best balance between performance and stability available?

David Lennon replied: As an oxychlorination catalyst the $CuCl_2$/KCl/attapulgite formulation has proven itself for many years' continuous operation within a large-scale refrigerant feedstock production chain.[1,2] A major advantage for its application in the current study (DOI: 10.1039/d0fd00014k) is its durability with respect to tolerance of the harsh conditions of the overall oxychlorination process. The catalyst used by Weber and co-workers in their report of a three-step reaction cycle for the

oxychlorination of CO to produce phosgene employed a KCl promoted CuCl$_2$ supported on silica.[3] Thus, the materials used in both studies are reasonably similar. However, given that hydroxyl groups associated with the attapulgite support material are thought to be active for the observed CO oxidation reaction (eqn (12); DOI: 10.1039/d0fd00014k), it may be informative to investigate alternative support materials.

Reflecting on the second question, the CuCl$_2$/KCl/attapulgite catalyst formulation is thought to represent a suitable balance between performance and stability. The former characteristic being verified by the ability of the catalyst to facilitate stabilised operation of the Deacon reaction within the micro-reactor arrangement utilised in the study, *e.g.* Fig. 8 in the paper (DOI: 10.1039/d0fd00014k). In light of positive outcomes reported by Weber and co-workers for CO oxychlorination over a similarly doped CuCl$_2$ catalyst, experimental parameters such as residence time and operation at elevated CO pressures are thought to be key to initiating sustainable reaction.

1 I. W. Sutherland, N. G. Hamilton, C. C. Dudman, P. Jones, D. Lennon and J. M. Winfield, *Appl. Catal., A*, 2011, **399**, 1–11.
2 I. W. Sutherland, N. G. Hamilton, C. C. Dudman, P. Jones, D. Lennon and J. M. Winfield, *Appl. Catal., A*, 2017, **471**, 149–156.
3 T. Zhang, C. Troll, B. Rieger, J. Kintrup, O. F.-K. Schlüter and R. Weber, *J. Catal.*, 2010, **270**, 76.

Peter W. Seavill communicated: My question is on your micro-reactor apparatus. As your current apparatus is geared towards mechanistic analysis and has helped to find efficient conditions for the production of phosgene, how easy/difficult would it be to modify your micro-reactor to use this phosgene generation for preparative reactions with other reagents?

David Lennon communicated in reply: The micro-reactor arrangement was specifically designed to investigate phosgene synthesis catalysis and is housed within the University of Glasgow's Chemical Process Fundamentals Laboratory. A comprehensive description of the apparatus plus the associated operating procedures is described elsewhere.[1] In addition to the oxychlorination studies presented at this (DOI: 10.1039/d0fd00014k) and an earlier *Faraday Discussions* meeting,[2] the facility has been used to examine more conventional phosgene synthesis catalysis over activated carbon.[3,4] This includes considering the matter of small quantities of bromine in the chlorine feedstock, which can result in the formation of species such as BrCl, COBrCl and COBr$_2$.[5]

The facility is equipped with a dedicated phosgene supply.[1] Although its primary role is as a calibrant, in principle, it could additionally be used as a reagent. Presently, the facility is only intended for use with gaseous reagents and products.[1] Phosgenation reactions involving liquid phase transformations would require some re-configuration of the existing set-up.

1 G. E. Rossi, J. M. Winfield, C. J. Mitchell, W. van der Borden, K. van der Velde, R. H. Carr and D. Lennon, *Appl. Catal., A*, 2020, **594**, 117467.
2 S. Guan, P. R. Davies, E. K. Gibson, D. Lennon, G. E. Rossi, J. M. Winfield, J. Callison, P. P. Wells and D. J. Willock, *Faraday Discuss.*, 2018, **208**, 67–85, DOI: 10.1039/c8fd00005k.
3 G. E. Rossi, J. M. Winfield, C. J. Mitchell, N. Meyer, D. H. Jones, R. H. Carr and D. Lennon, *Appl. Catal., A*, 2020, **602**, 117688.
4 G. E. Rossi, J. M. Winfield, N. Meyer, D. H. Jones, R. H. Carr and D. Lennon, *Appl. Catal., A*, 2021, **609**, 117900.

5 G. E. Rossi, J. M. Winfield, N. Meyer, D. H. Jones, R. H. Carr and D. Lennon, *Ind. Eng. Chem. Res.*, 2021, **60**, 3363–3373.

Ian Silverwood opened discussion of the paper by Yasushi Sekine: How does your suggested mechanism of proton motion on the catalyst surface differ from the conventional concept of hydrogen spillover?

Yasushi Sekine replied: In conventional hydrogen spillover, the driving force is the concentration of the hydrogen. In contrast, in our proposed mechanism, the proton is driven by an external DC potential, which is the crucial difference between the two.

Ian Silverwood asked: If the proton hopping across the support is driven by the applied voltage, do you expect the hydrogen atoms will travel further from the active metal that dissociates the dihydrogen molecule? Is this increased spillover the cause of the enhanced catalytic activity?

Yasushi Sekine responded: Yes, I think so. Thank you for your interest.

Collin Smith enquired: Is electronic promotion also important for the catalyst (*e.g.* ammonia synthesis) in addition to protons? You suggest you are able to add hydrogen to molecular nitrogen by applying excess of protons across the surface, but it is known that adding hydrogen to molecular nitrogen is very difficult. In fact, enzymatic nitrogenase, the most well-known route for this mechanism, uses high energy electrons. Do you see a role of electrons?

Yasushi Sekine answered: Thank you for your comments. I agree with you, and electronic promotion also plays an important role in this case. Local electrical-neutrality of the material is also important. The reaction equation only includes molecules (proton), but we have to mention the importance of electrons as well.

Philip Davies asked: Does the polarity of the applied field affect the outcomes of the experiment?

Yasushi Sekine replied: Thank you for your question. No effect of the direction of DC-electric field on the reaction.

Simon Kondrat enquired: Stoukides[1] and Vayenas[2] have researched electro-chemical promotion of catalysts or non-faradaic electrochemical modification of catalytic activity since the early 1980s. Can I ask how your process differs from theirs?

On a further point regarding EPOC/NEMCA. Can you differentiate the promotional effects seen by these techniques from the proton migration claimed in your mechanism? For example changes in catalyst work function/density of state changes?

1 G Marnellos and M. Stoukides, *Science*, 1998, **282**(5386), 98–100.
2 C. G. Vayenas, S. Bebelis and S. Ladas, *Nature*, 1990, **343**, 625.

Yasushi Sekine responded: It has been confirmed that changes in the work function and density of states of the catalyst do not occur in our system by *operando*-EXAFS. Therefore, it is due to proton hopping and collisions, not the change in work function of the supporting metal itself. This is also major evidence for the unusual observation of reverse isotope effects in HD exchange reactions.

Christian Hess asked: In your presentation you were focusing on surface processes. Can you exclude a contribution from bulk processes (*e.g.* ion mobility) on the reactivity behavior?

Yasushi Sekine replied: Thank you for your comments. The temperature is rather low, at around 423 K, so the bulk diffusion of proton and other ions are negligibly small from EIS data.

Megha Anand enquired: This process is different from the thermal process or the field effects we observe in electrocatalysis. How scalable is this process, for example for ammonia synthesis, and what problems/challenges do you foresee in scaling up?

Yasushi Sekine answered: When scaling up, the efficiency has been found to be rather good. At present, the knowledge of conventional solid catalytic processes can be applied almost directly to scale-up this reaction process.

Deniz Uner asked: Did you investigate the thermal effects induced by the presence of bulk resistance of the solid phase? Could there be a temperature gradient within the pellet?

Yasushi Sekine replied: In the case of steam reforming, external heating of 20 K at 423 K (*i.e.* at 443 K for the reaction temperature) cannot accelerate the reaction, so the thermal effect by the bulk resistance is not important. We cannot measure the temperature gradient within a pellet due to its small size.

Deniz Uner questioned: The difference of 20 K is not trivial and can induce some dramatic changes in the activity. Is it possible to re-evaluate the reported activities by making a correction for temperature?

Yasushi Sekine answered: Of course, 20 K is not trivial, but in some cases, it is very trivial for example methane steam reforming. As shown in the paper (DOI: 10.1039/c9fd00129h), we can decrease gas-phase temperature by applying the field of several hundred K. It is trivial.

Justin Hargreaves said: Thank you very much indeed for a very interesting presentation. In postulating an associative mechanism for ammonia synthesis, do you have any direct evidence for the involvement of a dinitrogen intermediate?

Yasushi Sekine responded: Thank you for your comments. Direct observation of the evidence (dinitrogen intermediate) is very hard. So far we confirmed it by DFT calculation.

Philip Davies asked: Fig. 3 in the paper (DOI: 10.1039/c9fd00129h) implies that the effect of the applied field is to increase reaction product yields above those expected from the thermodynamic equilibrium. What is changing to change the position of equilibrium in that way?

Yasushi Sekine answered: This is due to the irreversible reaction mechanism. It is described in the paper (DOI: 10.1039/c9fd00129h).

Ali Reza Kamali enquired: Very interesting work. I am wondering what was the size and the distribution of catalyst particles on the support in your work, and what would be the optimum size/morphology of the catalyst in your opinion? Also, what would be the properties of an ideal semiconductor material to serve as the support in your case?

Yasushi Sekine replied: Thank you for your interest and questions. Of course, the particle size is important, especially for the specific surface area and gas diffusion. Surface proton hopping itself does not depend on the particle size.

M. Bowker asked: What about the possibility of electric field effects on oxygen mobility at higher temperatures in oxidation reactions? I understand your response to non-faradaic electrochemical modification of catalytic activity (NEMCA) and not getting bulk diffusion of oxide ions, but what about surface oxygen movement and oxidation reactions. Could you use enhanced surface diffusion of oxygen species for reactions?

Yasushi Sekine responded: Thank you for your question. We have already confirmed the mobility of surface oxygen by applying an electric field, please see ref. 1 and 2, *etc.*

1 A. Sato, S. Ogo, K. Kamata, Y. Takeno, T. Yabe, T. Yamamoto, S. Matsumura, M. Hara and Y. Sekine, *Chem. Commun.*, 2019, **55**, 4019–4022, DOI: 10.1039/c9cc00174c.
2 S. Ogo, H. Nakatsubo, K. Iwasaki, A. Sato, K. Murakami, T. Yabe, A. Ishikawa, H. Nakai and Y. Sekine, *J. Phys. Chem. C*, 2018, **122**(4), 2089–2096, DOI: 10.1021/acs.jpcc.7b08994.

M. Bowker enquired: Is it possible have a phenomenon called micro-sparking in the catalyst bed? That is, at poor interparticle contacts where a voltage drop is established, a spark may create a local plasma, which would aid reaction?

Yasushi Sekine answered: We can confirm whether such local plasma exists or not by many analyses, emission spectra, isotope exchange experiments, *operando-*IR/EXAFS/XANES, *etc.* From this evidence, there is no such small plasma in our case.

M. Bowker opened discussion of the paper by Moritz Wolf: Is there any loss of Ga from the bed? Interesting material; Ga is liquid at room temperature, but with a low vapour pressure at reaction temperatures. However, it still has a certain vapour pressure, so do you actually see any gallium come out of the end of your bed?

Moritz Wolf replied: We did not detect significant loss of metallic gallium during alkane dehydrogenation in the temperature range of 450–600 °C. The Ga

content before and after catalytic application was comparable and potential loss limited to the accuracy of the metal analysis by means of ICP-AES. Compared to the metallic Ga^0, oxidised species are more volatile. In particular the formation of Ga_2O can potentially result in loss of gallium from the catalyst bed and may be formed as a volatile intermediate at temperatures exceeding the studied temperature range.[1] It has to be noted that the existence of a Ga_xO passivation layer has been reported for the as-prepared supported Ga-rich phases.[2] Hence, some initial volatilisation during *in situ* removal of this layer by formed H_2 during alkane dehydrogenation may be likely, but negligible when compared to the overall amount of Ga in the catalyst. For other low melting point metals, such as In, initial studies point towards potential leaching *via* formation of volatile hydride phases.[3] Conclusively, we currently consider the formation of volatile non-metallic species more critical than the evaporation of the liquid low melting point metals due to their corresponding vapour pressure at reaction temperature.

1 D. P. Butt, Y. Park and T. N. Taylor, *J. Nucl. Mater.*, 1999, **264**, 71–77.
2 M. Wolf, N. Raman, N. Taccardi, M. Haumann and P. Wasserscheid, *ChemCatChem*, 2020, **12**, 1085–1094.
3 P. Breisacher and B. Siegel, *J. Am. Chem. Soc.*, 1965, **87**, 4255–4258.

Nico Fischer asked: Can you please expand on the methodology you employ to make sure that the active phase is actually dissolved in the Ga and does not reside as individual moieties on the support's surface.

Moritz Wolf answered: After deposition of the metallic gallium droplets on the support, the noble active metal atoms are introduced *via* galvanic displacement. This technique ensures selective replacement of less noble gallium in the droplets by the active metal atoms and is consequently expected to prevent their deposition on the support material. The concentration of the active metal atoms in the Ga-rich droplets can be adjusted by their concentration in the solvent during this procedure.

Nico Fischer enquired: Once the Ga droplets are liquid, how mobile are they on the support? Do droplets meet and maybe aggregate? If they don't aggregate do you expect a gradual equilibration of the active metal concentration with time due to exchanges between droplets when "meeting"?

Moritz Wolf responded: This is an excellent question that addresses one of our current focus areas of study. Hence, we hope to provide precise answers in the near future. For now, we can report on a strong influence of the macroscopic morphology of the surface of the support material on the mobility and aggregation of droplets under reaction conditions. For example, rough surfaces seemingly prevent excessive redistribution of the liquid alloy droplets over the support. Contrary, the smooth surface of amorphous SiO_2 spheres may allow for strong interaction in-between the droplets. Macroscopic inhomogeneity, such as cracks, results in an accumulation of the droplets. Hence, the mobility greatly depends on the support material and we do expect aggregation of droplets to a certain degree. A gradual equilibration of the concentration of the secondary, active metal concentration in the bimetallic droplets throughout the catalyst would be a nice feature. However, we rather feel like the redistribution of active metal atoms is

more likely to occur *via* the formation and re-dissolution of bimetallic solid phases on the support.

Christian Hess asked: In the experiments a capillary was used. I was wondering how stable it is, considering it is moved through the reactor.

Moritz Wolf answered: Here, a stainless steel capillary was employed, which is actually fixated on both sides of the set-up to prevent bending and damage. The concept of the compact profile reactor enables movement of the heated reactor including the heating cartridge in the axial direction to allow for a relative movement of the catalyst bed with regard to the orifices of the capillary inside the catalyst bed.

Christian Hess enquired: For correlation of kinetic and spectroscopic data, is it necessary to switch between product and Raman analysis when using the capillary? How about temperature measurements? Which Raman excitation wavelengths can be (have been) used in this setup?

Moritz Wolf responded: Spatially resolved analysis of the gas phase and spectroscopy may be conducted simultaneously. The reaction gas was sampled *via* the internal capillary with orifices, while Raman spectroscopy was conducted using an external optical window directly exposing the catalyst bed inside the tubular reactor. The set-up allows integration of a thermocouple inside the capillary to additionally capture temperature gradients, which becomes particularly interesting in the case of exothermic reactions. In the presented study (DOI: 10.1039/d0fd00010h), a Raman excitation wavelength of 532 nm was employed, but the set-up generally enables a wide range of spectroscopic techniques.

Michael Claeys asked: Have you used longer chain alkanes? Would you expect any selectivity advantages with selective dehydrogenation resulting in preferential formation α-olefins?

Moritz Wolf answered: Indeed, we have studied the dehydrogenation of methylcyclohexane to toluene.[1] We observed a superior performance of a $Ga_{52}Pt/SiO_2$ SCALMS catalyst demonstrating a stable conversion and selectivity towards toluene at 450 °C and atmospheric pressure over 75 h time on stream. However, this dehydrogenation reaction targeting toluene does not provide any insight into a potentially favoured formation of α- or internal olefins. Unfortunately, a preferential formation of 1-butene was not investigated in the proof-of-concept study during dehydrogenation of butane.[2] In general, the formation of thermodynamically favoured internal olefins is expected rather than α-olefins, especially at elevated reaction temperatures. However, we do expect a hindered progressive dehydrogenation to dienes and trienes over SCALMS catalysts due to the dynamics of the liquid metal–gas interface.[2,3] After adsorption of the alkane and hydrogen abstraction over the active metal, the formed olefin is expected to rapidly move to the gallium, which is followed by rapid desorption of both products and consequentially hinders consecutive reaction steps. Further, the active metal atom dives back into the bulk of the Ga-rich droplet rendering it

inaccessible after desorption of H_2. Hence, re-adsorption also becomes less likely for SCALMS when compared to classical heterogeneous catalysts.

1 O. Sebastian, S. Nair, N. Taccardi, M. Wolf, M. Haumann and P. Wasserscheid, *ChemCatChem*, 2020, **12**, 4533–4537.
2 N. Taccardi, *et al.*, *Nat. Chem.*, 2017, **9**, 862–867.
3 N. Raman, *et al.*, *ACS Catal.*, 2019, **9**, 9499–9507.

Keith Whiston enquired: How might you practically regenerate these catalysts? What will their lifetime be on a per cycle basis? Eventually you will of course see coke build up. The main limitation of current commercially applied catalysts is their short cycle time and also overall lifetime in duty. How do you see these materials behaving after they have been regenerated several times?

Moritz Wolf responded: We have already demonstrated the feasibility of oxidative regeneration of a related Ga–Rh SCALMS after propane dehydrogenation at 500 °C.[1] Five consecutive cycles of 6 h of catalytic application and 2 h of exposure of the catalyst to air at 500 °C (flushing the system in-between) were demonstrated successfully and were accompanied by minor detrimental effects on the activity of the SCALMS. A certain degree of deactivation was only observed for the first three regeneration cycles, but the subsequent cycles gave almost identical results. This observation strongly points towards a feasible recyclability of the investigated SCALMS. No coke build-up was observed during this cyclic treatment. Such an oxidative cyclic regeneration is the objective of currently ongoing studies and represents a crucial step towards a potential commercialisation of SCALMS for short alkane dehydrogenation.

1 M. Wolf, N. Raman, N. Taccardi, M. Haumann and P. Wasserscheid, *ChemCatChem*, 2020, **12**, 1085–1094.

Keith Whiston asked: What do you think the optimum dehydrogenation cycle time would be for this catalyst to maximise the overall olefin yield?

Moritz Wolf answered: Obviously this strongly depends on the operation conditions. We are confident to extend the cycle time to several hours or even days, which would allow longer operation than for state-of-the-art catalysts, such as chromium-based systems.[1] However, we have not studied commercially relevant conditions yet, *e.g.* co-feeding of H_2 or increased concentrations of propane. While the latter is expected to result in accelerated deactivation, the presence of H_2 may be beneficial for extended cycle times.

1 Z. Nawaz, *Rev. Chem. Eng.*, 2015, **31**, 413–436.

Keith Whiston questioned: Do you see any acetylene formation at all from cracking on catalyst during the dehydrogenation cycle? This is a safety concern in commercial processes.

Moritz Wolf replied: No, we could not detect acetylene during propane dehydrogenation over the Ga–Pt SCALMS using SiO_2 as support material. However, this catalyst was shown to form less coke than Al_2O_3-supported catalysts and consequentially is expected to induce less cracking in general. Only low levels of

the cracking products ethylene and methane could be detected just above the detection limit of the employed product gas analysis (Fig. 7 in the manuscript (DOI: 10.1039/d0fd00010h)).

Deniz Uner enquired: Liquid metal systems offer unique opportunities to investigate surface thermodynamics, especially of the alloys, which is currently elusive for supported metals. Do you have plans for extending your experimental studies in this direction?

Additionally, liquid metals should be accessible to monitoring exchange between the bulk and the surface, could it be possible to monitor the surface vibrational states and elucidate the surface (and also bulk) free energies, using your model catalysts?

Moritz Wolf answered: To date, various techniques have been employed with our collaborators in the field of theoretical and physical chemistry to study the surface properties of the Ga-rich droplets in SCALMS. Exchange of metal atoms between the bulk and the surface is an important feature of SCALMS and the basis for the reported highly dynamic liquid metal–gas interface.[1,2] Firstly, angle-resolved XPS and *ab initio* molecular dynamic simulations both indicate depletion of the outer layer of the liquid Ga-rich droplet in secondary active metal, *i.e.* the active metal (Pd, Rh, *etc.*) is hiding in the bulk. Nevertheless, catalysis is feasible as the active metal atoms may pop up to the surface for potential interaction with molecules approaching the liquid metal–gas interface. The feasibility of such a dynamic behaviour has been demonstrated by means of infrared reflection-absorption spectroscopy and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) using CO as probe molecule, as well as DFT calculations.[2–4] In the case of propane dehydrogenation, propane may be adsorbed, followed by hydrogen abstraction and desorption of the products, after which the active metal atom dives back into the bulk of the Ga-rich droplet.[2]

1 N. Taccardi, *et al.*, *Nat. Chem.*, 2017, **9**, 862–867.
2 N. Raman, *et al.*, *ACS Catal.*, 2019, **9**, 9499–9507.
3 M. Kettner, S. Maisel, C. Stumm, M. Schwarz, C. Schuschke, A. Görling and J. Libuda, *J. Catal.*, 2019, **369**, 33–46.
4 T. Bauer, *et al.*, *ACS Catal.*, 2019, **9**, 2842–2853.

Conflicts of interest

There are no conflicts to declare.