

Catalysis for Fuels: general discussion

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Nico Fischer opened a general discussion of the paper by Nora de Leeuw: You have chosen Cu as a potential catalytic material and your calculations show that Cu is not the ideal surface to decompose hydrazine to H₂. Which materials would you be looking into in the future? Have you found any design parameters that should be followed?

Nora de Leeuw replied: We have made in-depth studies of three different mechanisms for N₂H₄ decomposition and these could be followed up using other potential catalysts, for example including Ir and Cu alloys.

Katherine Holt asked: In your model you neglect lateral adsorbate-adsorbate interactions. How can these be incorporated into the model and how would this in uence the results?

Nora de Leeuw answered: We could incorporate lateral interactions by ana-lysing the coverage effect. However, we have already reported previously that the interaction between species is insigni cant at less than 0.01 eV, except for N₂H₄ + CH₂, which is explicitly included in the microkinetic simulations.

Michael Bowker remarked: In Table 1 (DOI: 10.1039/C6FD00186F) there appear to be no net barriers in the adsorption-desorption processes from the gas phase. For example, dissociative adsorption of hydrogen (step R7) and desorption (step R6) have exactly the same energetics. It is known that this reaction is highly net activated from the gas phase, with very low sticking probabilities,¹ and hence the forward and reverse barriers are very different. This will have a signi cant effect on H populations on the surface and on H₂ production rates.

I. C. T. Rettner, D. J. Auerbach, and H. A. Michelsen, *Phys. Rev. Lett.*, 1992, 68, 1164.

Alberto Roldan responded: We have considered the reaction barriers for H₂ dissociative adsorption and associative desorption in the microkinetics simulation, although they are missing in the pre-printed version of the paper. We have now updated the paper to include these barriers.

Nora de Leeuw replied: The adsorption and desorption energies have the same absolute value and opposite sign. The activation energies of these processes are the ones that will show different values and they have been considered in the simulation process.

Emiel Hensen noted: The use of microkinetics modeling to predict the performance of different Cu surfaces in the decomposition of hydrazine is certainly a worthwhile approach. Within this approach, it is possible to interrogate the kinetics for the step(s) that determine the overall reaction rate as well as the steps that determine the selectivity. The latter may help to understand which aspect of the surface precludes formation of hydrogen.

An example of the use of the degree of rate control can be found in our work on CO hydrogenation on a Ru surface.¹ An example of the use of the degree of selectivity control and its derivation can be found in work on CO hydrogenation on Rh surfaces.²

1 I. A. W. Filot, R. A. van Santen and E. J. M. Hensen, *Angew. Chem., Int. Ed.*, 2014, 53, 12746–12750.

2 I. A. W. Filot, R. J. P. Broos, J. P. M. van Rijn, G. J. H. A. van Heugten, R. A. van Santen and E. J. M. Hensen, *ACS Catal.*, 2015, 5, 5453–5467.

Nora de Leeuw responded: Certainly, the microkinetic model employed here was derived entirely from computational results without any external parameters. This approach has been shown to be efficient and reliable.^{1,2} However, on a reaction network like the one presented here, it is not easy to find the rate limiting step and to analyze each degree of rate control will be extremely useful to find model descriptors.

1 A. Roldan, G. Novell, J. M. Ricart and F. Illas, *J. Phys. Chem. C*, 2010, 114, 5101–5106. 2 N. Y. Dzade, A. Roldan and N. H. de Leeuw, *J. Chem. Phys.*, 2013, 139, 124708–124708.

Thobani Gambu questioned: The simulated TPR (Fig. 2, DOI: 10.1039/C6FD00186F) seems to indicate that NH₃ coverage is zero (or trace compared to other species). Moreover, NH₃ production/desorption onset temperature coincides well with the decrease in N₂H₄ coverage. This may simply mean that NH₃ does not adsorb strongly enough on the Cu(111) surface and as a result it desorbs almost instantaneously upon formation from N₂H₄.

Therefore, could we potentially use the adsorption energy of NH₃ as a descriptor in screening for catalysts with improved H₂ yield/selectivity from N₂H₄? A similar approach has been presented in the literature.¹

1 J. K. Nørskov, F. Abild-Pedersen, F. Studt and T. Bligaard, *Proc. Natl. Acad. Sci. U.S.A.*, 2011, 108, 937–943.

Nora de Leeuw answered: We would like to analyse the degree of rate control to confirm that the adsorption/desorption is the limiting step in the production of H₂. We recognise that both the adsorption of NH₃ and H₂ are important rates in the evolution of hydrogen, but more analysis is still required.

Hans Niemantsverdriet enquired: From the point of view of making hydrogen, copper does not appear as a good choice, as the main product is ammonia. I wonder if it would make sense to look at metals known for decomposing ammonia, for which e.g. ruthenium is the best choice. On the other hand, this may not work either, because iridium is known as the best system for hydrazine activation. With that in mind, wouldn't it be useful to understand better why iridium is so special for hydrazine utilisation? Would you have any insights on this?

Nora de Leeuw responded: We initiated this project with the aims of explaining the use of hydrazine as a reducing agent in the synthesis of Cu nanoparticles. Certainly, exploring the reaction mechanism on Ir would be the next step to compare directly with the Cu and perhaps optimise the limiting rates using metal alloys to develop a more reactive catalyst.

Pieter van Helden said: Ir is an interesting metal, since it has C and O bond strengths in the same range as those of Co, Ni and Ru, while having a much lower H bond strength.¹ This would imply that it would quite easily liberate hydrogen gas, while maintaining the bonds to the other adsorbates at the operating temperature. This could be one of the features that makes it a good catalyst for the liberation of hydrogen gas from hydrazine.

1 J. Greeley and M. Mavrikakis, *J. Phys. Chem. B*, 2005, 109, 3460–3471.

Nora de Leeuw answered: That is right, the hydrogen adsorption cannot be strong if we aim to evolve H₂. However, other species adsorbing much more strongly than H can poison the catalyst or decrease its performance. We should seek for the right balance between the different adsorption energies.

Matthew Neurock said: This is an interesting reaction system. I have a comment and a question. The theoretical calculations that were carried out are consistent with the results we presented in our paper (DOI: 10.1039/C6FD00226A) in that the coordinatively-saturated Cu sites do not readily activate N–H bonds. The presence of NH₂^{*} species on Cu that form as a result of the activation of hydrazine, however, can act as a base and readily catalyze N–H bond activation via hydrogen transfer to NH₂^{*}. This, however, will more selectively lead to ammonia rather than H₂ production, as you found in your simulations. Iridium, which is used experimentally, however, will readily activate N–N bonds of the partially dehydrogenated N₂H_x species as well as the N–H bonds, thus allowing for the activation of hydrazine and the formation of hydrogen as a product. More active catalytic materials to form H₂ would likely require metals or metal alloys that have higher N^{*} binding energies and can activate N–N as well as N–H bonds and allow for facile H recombination. My question concerns a comparison of the experimental results and those from the simulations carried out at higher temperatures.

The N₂ production from the simulation appears to be about 10% lower than that reported experimentally. Can you speculate what the differences may be due to? Is this possibly due to the role of coordinatively unsaturated Cu sites that can more readily activate N–H bonds but are not currently included in the simulation?

Nora de Leeuw replied: That is what we believe. The surface in our model is ideal, without vacancies, ad-atoms, steps and any other defects that would modify the coordination and the electronic structure of the substrate. These low-coordinated atoms accumulate electron density and could bind N* stronger than high-coordinated ones (at the terrace), favouring the deprotonation process. The 10% disparity with the experiment may be due to the methodology and approximations taken into account: exchange–correlation functional and transition state theory among others.

Richard Catlow commented: The methodology you have developed is clearly powerful and predictive. Could you now apply it to other metals and alloys to identify which might be most effective. I am not suggesting a large scale screening exercise, but rather a focussed study of a number of systems which we expect to be promising.

Nora de Leeuw responded: That is correct; the next step would be identification of the degree of rate control, focussing only on the parameters modifying the steps that largely control the kinetics and selectivity of the process. In this way, we would significantly reduce the computational cost.

Paul Collier remarked: As a comment, this paper makes an interesting comparison between two modes of operation for hydrazine decomposition: batch and flow reactor. There is often great interest in which type of operation is best in other processes and perhaps DFT can illuminate this debate. Additional question: in reality, copper would be used as a supported catalyst in this process (such as Cu/Al₂O₃ or Cu/SiO₂). How would you expect this to change the modelling results, if at all?

Nora de Leeuw answered: Thanks for the comment. I would like to add that different sections of the flow reactor can be explored considering different amounts of products, e.g. an early section of the reactor will not contain products in the inlet flow, while late sections of the reactor will have small quantities of reactants. The validity of our model in a real supported catalyst depends on the extension of non-defective (111) terraces on the Cu particles. Small particles would have vertices and other defects with reactivity not included in our model.

Thabiso Perfect Oscar Mkhwanazi enquired: Have you investigated how the change of supports influences the metal charge transfer of copper and the effect of this charge density or transfer on selectivity? Can one take advantage of this charge transfer to select a specific product?

Nora de Leeuw replied: We have focused on Cu only but we agree that the charge transfer from the metal to the adsorbed species will influence their interaction and, therefore, the conversion and selectivity.

Ding Ma opened a general discussion of the paper by Matthew Neurock: As the processes share similar intermediates; is there a way to control the selectivity to selectively get one of the products?

Matthew Neurock replied: Controlling selectivity is somewhat of a challenge as aldol condensation and esterification both proceed through the direct reactions of propanal and propoxide intermediates in the rate controlling step. One could examine other metals, which would alter the binding energies or binding configuration of the propoxide or propanal, in an effort to increase the selectivity. I suspect that it would be easier to alter the selectivity by changing the binding energies of propanal rather than those of the propoxide, as C α -H activation and nucleophilic attack on the propanal occur at different sites on the molecule. A second and perhaps more sensitive approach would be to change the nature of the support, which would allow you to carry these reactions out at different sites.

Avelino Corma asked: In proton abstraction, the type of metal and support can be selected to maximise the reaction. Can you look at the nature of the interactions and the efficiency?

Matthew Neurock replied: Indeed, the activation of the weakly acidic C α -H bond is critical for the condensation reaction and this can be influenced by the metal as well as the support. We can carry out calculations on both the metal as well as the oxide separately to explore the binding energies as well as the activation barriers and overall reaction energies for the proton abstraction step. We can also examine the metals anchored to the support and explore the activation at the interfacial sites. In addition to the adsorption, reaction energies, and activation barriers at these sites, we can also examine how charge is transferred in the reaction to provide more mechanistic insight into how to drive this reaction.

Graham Hutchings enquired: Alcohols are being used as models for biomass, but biomass has many O atoms present; what happens if you use a diol rather than an alcohol? Would dehydration occur preferentially with a 1,2-diol?

Matthew Neurock responded: Previous experiments with 1,3-propanediol over Cu/ZnO/Al₂O₃¹ show that the diol undergoes both dehydration and dehydrogenation to form equilibrated mixtures of propene,² propen-1-ol, acrolein, as well as C₅-C₆ type oxygenated products presented here. The ZnO/Al₂O₃ support used in this work, however, can also catalyze similar reactions.

For 1,2-propanediol, I would suspect dehydration to predominantly occur at the secondary C center to form 1-propanol, as the formation of a secondary carbenium ion intermediate would be more stable than the primary intermediate. The dehydration reactions, however, may be occurring over sites on the ZnO/Al₂O₃ support and not on Cu/SiO₂. As such, the nature of the oxide support can play an important role in controlling the selectivity for specific products as it can actively carry out different reactions. In terms of dehydrogenation, I would suspect that the terminal CH₂OH groups are selectively dehydrogenated, as there is less steric hindrance for the metal to attach to the C-H bonds. This is consistent with previous experimental results for base (OH⁻) catalyzed oxidation of glycerol over Au, which show the selective dehydrogenation at the terminal hydroxyl sites and

the absence of dehydration.¹ This is also in line with other previous theoretical and experimental work that shows the metal catalyzed dehydrogenation preferentially occurring at the terminal CH₂OH sites. This, of course, is a speculation for the Cu system examined here.

1 W. C. Ketchie, M. Murayama and R. J. Davis, *Top. Catal.*, 2007, 44, 307–317. 2
M. Ide, B. Hao, M. Neurock, and R. J. Davis, *ACS Catal.*, 2012, 2, 671–683.

Michael Bowker asked: Propanal is weakly bound at ~ 28 kJ mol⁻¹, so it is physisorbed and difficult to activate. Do you think, as water is being produced in this reaction, it can have an impact on the binding of such species and the selectivities, and can you calculate these? Maybe the OH present can act as a base-promoter in these reactions? What is the binding energy of the propanol?

Matthew Neurock responded: Little water is produced in this reaction as esteri cation proceeds without the loss of oxygen and the predominant aldol condensation path proceeds via decarbonylation/decarboxylation with loss of oxygen as CO or CO₂. The results show that about 10% of the products would lead to the formation of water.¹ Water is thought to be activated on Cu (similar to propanol) and forms a basic surface hydroxyl that can carry out the same nucleophilic attack or H abstraction as the alkoxide on Cu, which is consistent with your statements. We reported in the manuscript (DOI: 10.1039/C6FD00226A) that the OH* groups are somewhat more basic than the alkoxide intermediates and show that the barrier to activate the weakly acidic C–H bond on the bound propanal is ~14 kJ mol⁻¹ more favorable than that of the alkoxide. We calculated the binding energy for propanol to be 29 kJ mol⁻¹.

1 M. E. Sad, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2011, 133, 20384–20398.

Enrique Iglesia added: The reactions were carried out in the presence of H₂ and we observed no detectable deactivation. The kinetic response is consistent with a limiting step mediated by a bimolecular transition state for both condensation and esteri cation.¹ We observed no effects of water, suggesting that neither O* nor OH* are involved as nucleophiles.

1 M. E. Sad, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2011, 133, 20384–20398.

Abhishek Kumar Gupta asked: Can Cu nanoparticles be used as a catalyst for trans-esteri cation of vegetable oil or waste oil? Can we synthesise fatty acid methyl esters or biodiesel from vegetable oil or waste oil?

Matthew Neurock answered: In theory, yes, as the base-catalyzed trans-esteri-cation in the homogeneous phase proceeds via the formation of an alkoxide of the carbonyl carbon on the ester, thereby, replacing the existing –OR group on the ester. This is very similar to the esteri cation mechanism observed on Cu, where the alkoxide ion attacks the carbonyl carbon, thus forming a C–O bond. There are various studies of Cu supported on basic oxides such as Cu/ZnO¹ and Cu/Mg/Al,² which carry out this chemistry. The Lewis base and acid sites on the support likely contribute significantly to the reactivity.

Evjeny Redekop queried: Aldol condensation (e.g. adsorbed propoxide and propanal) involves an elementary step with two adjacent oxygen-bound intermediates. How will the mobility of such intermediates affect the probability of their co-location on the Cu surface under the reaction conditions?

Matthew Neurock responded: Propanal and propoxide are thought to be present at high coverages on the surface. In addition, propanal and propanol are shown to be rapidly equilibrated on the surface. As such propanal and propoxide would be equilibrated and there should not be any issues concerning mobility.

Paul Collier remarked: (a) In the industrial process of acetylene hydrogenation, oligomerisation of reactive species leads to fouling of the catalyst by green oil formation. Are there any parallels between this and catalytic esterification/condensation?

(b) The results of your study are impressive; how might this learning be incorporated into a catalyst design led approach to develop new catalysts?

Matthew Neurock responded: (a) Aldol condensation and esterification reactions are carried out in the presence of hydrogen. The hydrogen tends to prevent or suppress the formation of more unsaturated intermediates, C–C bond formation and hydrocarbon chain growth. For reactions carried out over Cu/SiO₂, the hydrogen appears to prevent the continued chain growth as the reaction appears to stop at the coupled C₅–C₆ products. (b) Our results indicate that we want to use group 11 metals (Cu, Ag, Au) as well as large particles with highly coordinatively saturated metal sites, as this weakens the binding energy of the alkoxide, thus increasing its basicity and its ability to activate the weakly acidic C_α–H bonds and the nucleophilic attack on the carbonyl group. One could also look at moving to metal alloys to not only improve the activity but also enable increases in the selectivity. One could look at the binding energy of a probe alkoxide as well as perhaps the charge on the alkoxide to provide descriptors for the reactivity. Weaker alkoxides and higher degrees of electron density on the alkoxide would suggest more basic and reactive alkoxides. One could then readily screen a wide range of metals, metal alloys and different potential surface structures. The differences in selectivity are more challenging, as both condensation and esterification proceed via the same intermediates. One could use instead the overall reaction energies of the C_α–H activation and nucleophilic attack reactions to discern the most active metals and sites. One can and should analyze the influence of the oxide support. This would require more detailed calculations, however, to probe the individual elementary C_α–H and C–O formation steps.

Graham Hutchings remarked: Following on from the discussion point raised by Paul Collier on catalyst design, you mentioned that the small nanoparticles are less effective than the larger nanoparticles. This implies that the peripheral sites are not effective; is there a reason for this? Also it means we need to design catalysts where we have a range of atoms as a large nanoparticle does not use the metal atoms very effectively.

Matthew Neurock replied: Experimental results show that the turnover rates for propanal condensation and esterification rates carried over Cu/SiO₂ increase linearly as the Cu cluster sizes increase from 5 to 15 nm and level out as sizes > 20 nm.¹ Both aldol condensation and esterification reaction rates are controlled by the reactions between a surface alkanal and a surface alkoxide. The rate controlling step for esterification involves C_α-H activation of the propanal via the surface propoxide, while esterification proceeds via the nucleophilic attack of the alkoxide on the bound alkanal. The weakly bound alkoxide acts as a base that can abstract the weakly acidic C_α-H hydrogen of propanal in the rate controlling step for the condensation reaction, or carry out a nucleophilic attack on the carbonyl of the bound alkanal in the rate controlling step for esterification. The basicity and reactivity of the alkoxide are controlled by the binding energy of the alkoxide to the metal surface, where the more weakly bound alkoxides are more basic and reactive. The binding energies are controlled by the coordination number of the metal to which the alkoxide binds. Increasing the particle size increases the number of the more basic and more reactive coordinatively saturated low index terrace sites over the less basic and less reactive corner and edge sites. This is analogous to the high reactivity of large Au particles for oxidation when carried out in the presence of base. In terms of design, this would require increasing the number of coordinatively saturated sites. In order to save on the use of an expensive metal, one could think of the ratios of metal atoms as you propose, or core-shell particles where the active metal is deposited on a high surface area support or core.

1 M. E. Sad, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2011, 133, 20384–20398.

Mzamo Shoji communicated: Since TiO₂ exhibits both basic and acidic sites, could it be a better support than SiO₂ for the aldol condensation and esterification reactions?

Matthew Neurock communicated in reply: TiO₂ is known to readily carry out the aldol condensation but deactivates as result of carbon buildup. Cu supported on TiO₂ is indeed a very good catalyst as Cu aids in the equilibration of alkanals and alkanols, dehydrogenation of unstable hemiacetal intermediates and hydrogenation of the unsaturated intermediates that lead to carbon build up that otherwise deactivate the TiO₂.¹

1 S. Wang, K. Goulas and E. Iglesia, *J. Catal.*, 2016, 340, 302–320.

Letisha Deeplal communicated: To what extent would the support contribute towards aldol condensation? For example, γ-Alumina is known to be amphoteric, which can promote acid and base catalyzed aldol condensation.

Matthew Neurock communicated in response: In the reactions discussed here, SiO₂ was used as a support, thus allowing us to rule out the reactions that might come from the support. Indeed, many of the oxide supports with acid and base sites can also contribute to the activity. In more recent efforts, Cu/TiO₂ was used to take advantage of moderate Lewis acid–base sites on TiO₂ to carry out C–O and C–C bond formation, whereas Cu carried out the facile hydrogenation and dehydrogenation steps to equilibrate the alkanal + H₂ and alkanol mixtures, and to avoid deactivation

by the formation of higher hydrocarbons. There are a range of other oxides that can also be used to take advantage of the sites on the metal and the oxide.

Letisha Deepal communicated: How applicable would this study be towards the selective hydrogenation of α,β -unsaturated aldehydes, whereby the adsorption and activation of either the C=C or C=O bond can be controlled?

Matthew Neurock communicated in reply: A few of the mechanistic concepts in this work are similar to those involved in selective hydrogenation. On most transition metal surfaces the atomic hydrogen that forms extracts electron density from the surface and becomes hydridic. The hydride can act as a base and carry out nucleophilic attack on the carbon of the C=O (or C=C) to form an alkoxide (or alkyl) species similar to the rate controlling attack of the alkoxide on the C=O in the esterification reaction. The most active metals are those that bind hydrogen strong enough to allow for H₂ dissociation but weak enough to allow hydrogen to add to the carbon or the oxygen. This is consistent with the surfaces necessary for esterification and condensation, which require metals that can activate H₂ but are weak enough to allow the alkoxide to behave as a base. The subsequent addition to the oxygen, however, would be different as it would involve the addition of a positively charged hydrogen, together with an electron transfer.

Hans Niemantsverdriet opened a general discussion of the paper by Tracey van Heerden: Your work is very useful to get a feel for what a support in combination with a metal might do. It looks like the O–Al–(OH)₂ moiety acts a bit like a potassium promoter. It sets up a dipole on the surface, which somewhat weakens the C–O internal bond, and as a result you find a stabilisation of the CO adsorption plus a slight weakening of its internal bond. The activation energy for dissociation is a bit lowered, although probably not enough to break it, as the entropic advantage of desorption is hard to beat. Nevertheless, the result provides valuable insight. Do you have any insight into what would happen if instead of this molecular Al species, you had a more extended island of Al₂O₃ (perhaps OH terminated) on the cobalt surface? I noticed that the Al in your cluster is not quite in the 3+ state, while it would be in Al₂O₃. Would we still see similar effects for CO bonded adjacent to such Al₂O₃ islands?

Tracey van Heerden responded: I can only speculate with this question. I expect that with a more extended island of alumina we would encounter a reduced effect. Partially due to the different environment the Al finds itself in, partially due to the Al being in the 3+ state in the island like you mentioned. I would also wonder though if the CO would still have as easy access to the metal centre of the Al on an extended island than what it does on the ligand, in order for it to be affected in the first place.

Nico Fischer remarked: In your paper you discuss the different types of ligands you have investigated as models for metal support interaction based effects on activity and selectivity. In a realistic supported cobalt catalyst, where would these ligands be found? Do you think they – or similar species – might exist at the metal support interface, or are there other formation mechanisms possible? Also, how mobile would these species be under realistic FTS conditions, i.e. could they

possibly migrate to the edge and kink sites and possibly block certain active centers there?

Tracey van Heerden replied: We know from laboratory work that on an inverse catalyst, the alumina based ligands are highly dispersed and do not form segregated amorphous alumina. Some calculations on edges and kinks are still needed to truly determine the location of these ligands, as it is feasible that they may occupy active centres at these sites. It is worth noting though that experimentally the inverse catalysts show increased activity when the loading of the support-based ligand is increased. On a real catalyst, one of the formation mechanisms being proposed is the dissolution of the support during the wet chemistry steps, which then deposits back onto the support or the metal oxide during drying, with it having been demonstrated that the reduction of the metal oxide does not destroy these ligands.

Pieter van Helden noted: This is a very interesting approach that has been presented here with a lot of future potential in studying promoter/support interface effects. The presented charge density difference plots remind me somewhat of early computational work on how potassium atoms bind to oxygen atoms on a Rh surface.¹ The key there was also the direct bonding interaction and charge transfer. Typically for promoters, changes in the electronic structure of the metal are invoked, but here there seems to be a direct bond-forming interaction. Looking at a typical Co catalyst, the Co is present as nanoparticles (NPs), with a significant percentage of exposed defect/step sites. Here you show Alumina ligands on a single Co surface. However, if these ligands were to bind to some of the defect/step sites on a realistic Co NP, would it still have the same effect on CO? Would it not bind stronger to these sites and poison the sites?

¹ Z.-P. Liu and P. Hu, *J. Am. Chem. Soc.*, 2001, 123, 12596–12604.

Tracey van Heerden answered: It is possible that the ligands may prefer to bind to defect/step sites, however, inverse catalysts that were produced in the lab show a net positive influence of these ligands on the CO dissociation, so it is evidently not a simple matter of poisoning when working on realistic NPs.

Michael Bowker said: I am impressed by this work and approach. Sometimes we think of inverse catalysts as 'model' catalysts, but of course they are not. Ammonia synthesis Fe catalysts (and Fe FT catalysts) have minor components of Al and K (and others), which preferentially segregate to the surface. They are unusual in having very high levels (~95%) of the active metal component in the catalyst. Although Al is often called a 'structural promoter' it must act in a very different way from a traditional support and have more than one role. It may be that, since it is intimately connected with the surface, it has a specific chemical role. Thus, the work examining the influence of oxidised Al species on reactivity is quite relevant to 'real' systems.

Simon Kondrat remarked: Fischer–Tropsch synthesis involves aggressive reaction conditions that will likely change the metal–support interaction. Do you feel your model reflects the possibility of an alumina overlayer under reaction

conditions? Or does the non-reducible nature of alumina make this unlikely? An example of this effect is the Cu–ZnO methanol synthesis catalyst system, where there is evidence that under reducing conditions Zn or ZnO_x forms at the Cu particle interface.¹

1 M. Behrens, F. Studt, I. Kasatkin, S. Kuhl, M. Hävecker, F. Abild-Pedersen, S. Zander, F. Girgsdies, P. Kurr, B. Knief, M. Tovar, R. W. Fischer, J. K. Nørskov and R. Schlögl, *Science*, 2012, 336, 893–897.

Tracey van Heerden responded: Yes, it is unlikely due to the nature of the support. It is much more likely that a support like titania would form overlayers on a Co FT catalyst, whereas alumina and silica would not.

Emiel Hensen continued: The presented work describes a novel approach to tune CO dissociation on a cobalt surface. It links to other approaches where for instance a reducible oxide is used to increase the rate of CO dissociation. In this particular case, the coordinative unsaturation of the AM₂ ligand can explain the lowered CO dissociation barrier. It would be worthwhile to compute the regeneration of the active site by removing the O atom of the Lewis acidic Al site. Was this route explored? What are the typical barriers?

Another approach following the suggestion of Prof. Niemantsverdriet would be to explore patches of aluminium oxide which contain Al atoms at their edges with a lower degree of coordinative unsaturation.

Tracey van Heerden replied: This route is currently being explored, so I cannot yet comment on typical barriers. The suggestion of Hans Niemantsverdriet is I believe computationally too expensive to be properly explored at this point.

Alberto Roldan remarked: As you showed in the pictures, the presence of Al activates the CO bond (the C–O distance increases). Is it an effect of the Al low coordination? Do you think CO will also be affected at the interface where the particle-support mismatch may affect the Co–Co distance and electronic structure?

Tracey van Heerden answered: I do believe CO would be similarly affected at the interface, even with possible effects on the Co structure. The interaction is very direct between the ligand and the CO and may well be somewhat due to the Al coordination.

Graham Hutchings addressed Tracey van Heerden and Paul Collier: What happens if you start with a preformed Co/SiO₂ or Co/TiO₂ catalyst, perhaps you would expect a positive effect by adding the aluminium complexes to these catalysts? I would expect this to be an easy experiment to try and would provide support for the effect you are proposing.

Paul Collier responded: Decorating the cobalt surface with different well-defined aluminium complexes is an interesting idea. If these could be tailored to sit on specific cobalt sites it might be possible to influence the process positively as described.

Tracey van Heerden replied: Yes, I would expect a positive effect.

Matthew Neurock commented: Your calculations show that Al may play a role in activating the CO bond. The model that you have used, however, involves a 3-coordinate Al site that binds to the O of CO. I would expect the Al–O bond here to be rather strong as the Al site is coordinatively-unsaturated. While this would aid in the initial activation of the CO bond, these sites would be very difficult to regenerate the 3-coordinate Al, as the Al–O bond is much stronger than the 4- or 5-coordinate Al–O bond. As such, these sites would be difficult to regenerate. In addition, your theoretical results show that while the CO is more strongly held to these sites, the barrier to activate the CO* is a little higher than that on the Co surface alone. Since CO is covering the surface, the activation barrier would be measured from the lowest adsorbed CO–M2 state (~ 2.25 eV) to the TST (~0.25 eV), which is about 2 eV. This looks to be higher than the barrier to dissociate CO* on Co (solid core), which is about 1.7 eV.

Tracey van Heerden responded: I found that the 3-coordinate M2 ligand was more stable than the 4- and 5-coordinate ligands, indicating that regeneration is possible.

Simon Kondrat asked: In the paper you discuss the effect of the aluminium ligands affecting the structure of the Co nanoparticle, and so changing the exposure of (111) and (100) planes. In your opinion, how significant is this effect?

Tracey van Heerden replied: The very simple calculations I presented show a significant effect on the structure of a Co nanoparticle. With a more realistic inclusion of particularly the edge sites, and the inclusion of a high CO coverage, this effect may be less severe.

Mzamo Shoji communicated: What difference would you see, if any, on your ligand valence charge according to Bader charge analysis if you used a silica based ligand?

Tracey van Heerden communicated in reply: I do not yet have results on the Bader analysis of the silica system, however I can say that the stable geometries differ to those of the alumina system, and so I do expect there to be differences in the characterization as well.

Michael Claeys communicated regarding the paper by Enrique Iglesia: You describe a rate equation which is applicable to cobalt and ruthenium based FTS. For iron based FTS we normally need to include a water term in the denominator to account for the inhibiting effect of water with these catalysts. In your opinion, is the mechanism on iron based catalysts fundamentally different compared to that on cobalt or ruthenium, or is the above merely a reflection of the dynamic interplay between magnetite and carbide, which is determined by local water to syngas ratios? This was also noted by B. Jager et al.,¹ where he stated that: "It may occur during macrokinetic studies, that the wide experimental range – statistically necessary – of the concentration of reactants used, leads to surface changes

in the catalyst. In that case the selection of the 'best' rate of reaction based upon the least squares criterium becomes merely a statistical exercise."

I B. Jager and R. Espinoza, *Catal. Today*, 1995, 23, 17–28.

Enrique Iglesia communicated in reply: Indeed, the effects of water, both as an inhibitor and as an occasional promoter of Fischer–Tropsch synthesis rates, differ among Co, Ru, and Fe. The rate equations to which I refer have been typically reported based on data at differential CO conversion and thus low prevalent water pressures relative to those of CO and H₂. These inhibition effects are stronger in Fe than in Co and even weaker on Ru, the expected trend from their oxygen binding energies and their noble/base character. In the case of Fe, the complex-ities of such surfaces during catalysis and their exchange of C and O with gaseous species during turnovers makes their surface composition and possibly even their surface and bulk structures sensitive to the O and C chemical potentials imposed by the elementary steps required for turnover and their reversibility. As such Langmuirian treatments become o en an exercise in statistical analysis. This is what I showed in my lecture (DOI: 10.1039/C7FD00018A) by the inconsistency between the ability of such rate equations to accurately describe measured rates at FTS conditions, but with adsorption constants for CO that represent mere statistical ts and are unrelated to the CO adsorption properties of such surfaces as a result of the dense adlayers present during catalysis.

Neil Coville opened the general discussion: The use of hydrazine as a ligand has been explored e.g. in organometallic chemistry over many years. If I remember, they can even form dimers. Do your studies allow for these different complexes in your mechanism? Are they ruled out? The early studies may also provide information on M–N₂H₂ interactions?

Nora de Leeuw responded: We have previously investigated the assembly of up to 9 hydrazines on Cu surfaces with multiple arrangements.¹ The interaction between them is very small (<0.01 eV) and it will not in uence in the microkinetic model. However, comparison with organometallic clusters would indeed be interesting.

I S. S. Tafreshi, A. Roldan and N. H. de Leeuw, *Surf. Sci.*, 2015, 637-638,140–148.

Nico Fischer continued: From DFT based studies preferred reaction mecha-nisms can o en be postulated. From these results, can active site requirements be deduced, extending beyond the ideal surface? If so, could these aid experimen-talists in the actual design of catalysts?

Nora de Leeuw replied: From reaction mechanism and electronic structure calculations we can nd predictors that direct the limiting rates. The extrapola-tion of these predictors to defects on pure and alloy systems should be possible.

Matthew Neurock added: The insights on the nature of the active sites can be used to help aid in future design efforts. While I did not discuss the results, we have shown in the manuscript (DOI: 10.1039/C6FD00226A) that the binding of the

alkoxide is over 26 and 40 kJ mol⁻¹ stronger at the coordinatively unsaturated step and corner sites. The stronger binding energy leads to much less basic surface intermediates and significantly higher barriers for carrying out the rate determining C–H activation and nucleophilic attack. This suggests that these sites are not active in carrying out the catalysis. This is consistent with the experimental results that show that small particles are much less active than the larger particles and that the rates increase with increasing particle size, as the larger particles increase the number of coordinatively saturated terrace sites.¹ The results indicate that the most active sites are those that are coordinatively saturated and weakly bind the alkoxide, thus allowing the alkoxide to behave as a base. One could potentially increase catalytic activity by moving to Ag or Au, alloying Cu, Ag or Au with other metals, or producing core-shell metal alloys, which decrease the binding energy of the alkoxide and increase its basicity and reactivity. In addition, one could also improve activity and selectivity by altering the support to create ideal bifunctional sites.

1 M. E. Sad, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2011, 133, 20384–20398.

Neil Coville remarked: The use of the alkoxy group on the surface is proposed to act like an alkoxy group in a homogeneous base-catalysed organic reaction; how do organic chemists perceive this use? The idea is that staying bound to the surface impacts on the alkoxy group but that it still acts like a base. It seems then that there is a spectrum in using OR⁻ (i.e. unattached) to surface bound OR. One could imagine that ion-pairing, for instance, would also modify this interaction and hence lead to variations in activity. Can this variation be exploited in terms of activity/selectivity?

Matthew Neurock answered: I don't know how the organic chemists would perceive this, but I suspect favorably as the mechanisms proposed are consistent with classic base-catalyzed organic reactions in solution as well as in homogeneous catalysis. In the organic systems, the reactive alkoxide intermediates are stabilized by their interactions with the solvent as well as the cation. In the gas phase work carried over Cu discussed herein (DOI: 10.1039/C6FD00226A), the electron-rich metal surface acts like the solvent and the cation as it allows for charge transfer to and stabilization of the alkoxide intermediate.

You raise a very interesting point in that one way in which to begin to tune the reactivity would be via the cationic promoters. For the gas phase reactions discussed herein, metal cations in the form of MO_x clusters deposited on the surface or on the support may be used to promote the reaction or participate themselves in carrying out the reaction. This is similar to what happens for Cu supported on basic metal oxide supports such as TiO₂, ZrO₂ and MgO, where these supports themselves can readily carry out the reaction.¹ The reactions can also be carried out in the liquid phase, where one can indeed generate alkoxide ions that may participate in solution reactions. We have discussed such solution phase and surface reactions for the oxidation of alcohols and carbonyl compounds over supported Au particles in the presence of base and aqueous media.² This would open up a number of opportunities in which one could engineer the active sites to control activity and selectivity.

Enrique Iglesia enquired: Is your microkinetic model accurate enough to explore the following possibility: explore the best catalysts for the reverse reactions – the synthesis of hydrazine from N_2 and H_2 – then combine the most optimal catalysts for these reactions with those that you have discarded as useful for hydrazine decomposition because they form ammonia? This would provide for a bifunctional system to form ammonia from N_2 and H_2 , possibly at temperatures much lower (and also at much lower pressures) than in current practice. The two functions would not have to co-exist in the same catalyst particle because hydrazine would act as a molecular shuttle between functions residing within diffusion distances.

Nora de Leeuw answered: This is a very interesting point worth exploring. Indeed, using principal component analysis and limiting rate control techniques may give us the properties of these catalysts.

Graham Hutchings addressed Nora de Leeuw and Enrique Iglesia: Following on from the point raised by Enrique Iglesia concerning the possibility of finding a low pressure, low temperature route to ammonia, from Fig. 7 of Nora de Leeuw's paper (DOI: 10.1039/C6FD00186F) it is clear there is a facile route from hydrazine to ammonia. Taking into account the comment by Hans Niemantsverdriet that Ir is a much better catalyst than Cu for the reaction, perhaps an alloy of Ir would be a good starting point. However, the second component would need to activate nitrogen and hydrogen.

Nora de Leeuw responded: This is an interesting point worth considering. We could move to the formation of NH_3 , which also has commercial interest, or the formation of H_2 by alloying different metals, preferably cheap ones, whose properties and the selectivity for each process.

Ding Ma opened a general discussion of the paper by Kees-Jan Weststrate: What will happen if you begin with CH_3I or $CH_3 + CO$? Will CO dominate the surface?

Kees-Jan Weststrate responded: We have not yet performed experiments for the CH_3/CO system in the absence of extra surface hydrogen. This informative experiment would provide interesting information on how CO affects dehydrogenation of CH_3 as well as the coupling reaction.

David Lennon asked: In Fig. 1(c) (DOI:10.1039/C6FD00191B) you present the RAIRS spectrum for CH_3I on Co(0001) which corresponds to the symmetric deformation mode of adsorbed methyl groups.

(i) Did you see any evidence for other CH_x species in these RAIRS measurements?

(ii) Did you examine CH_2Cl_2 adsorption on Co(0001) by RAIRS? If so, did you see any evidence for adsorbed methylene species?

Kees-Jan Weststrate responded: (i) The RAIRS experiment only showed the presence of methyl species and we did not resolve any other intermediates such as CH or acetylene. This could be due to the relatively poor signal-to-noise ratio in the CH_x stretching region. We did not, for example, get a clear signal for the CH_3 -related stretch vibration. Both CH and acetylene would only have vibrational bands in this region.

(ii) We did not perform IR experiments using CH_2Cl_2 . It is however expected that CH_2 groups are highly reactive and would be difficult to observe in significant concentrations.

Paul Akomeah remarked: To what extent has research on Fischer–Tropsch synthesis been carried out by replacing H_2 with D_2 and what were the findings, if any?

In case the reaction of D_2 with CO turned out well, what would be the fate of the resultant fuel obtained? Have such fuels been used in machines before and what was their effect on the systems they were used in?

Kees-Jan Weststrate responded: When hydrogen is replaced by deuterium, the CO conversion activity typically increases and the chain growth probability increases as well, see e.g. ref. 1. I am not aware of studies where deuterated FTS products have been produced in high enough quantities to be used as fuels, as such studies are typically done to obtain fundamental insights. From the perspective of surface reactions, replacing hydrogen by deuterium has an impact in various ways. Due to the higher mass of D_2 compared to H_2 , the collision frequency at a given pressure will be 1.4 times smaller. Thermal desorption experiments from a $\text{Co}(0001)$ surface, Fig. 1, show that deuterium desorption via 2

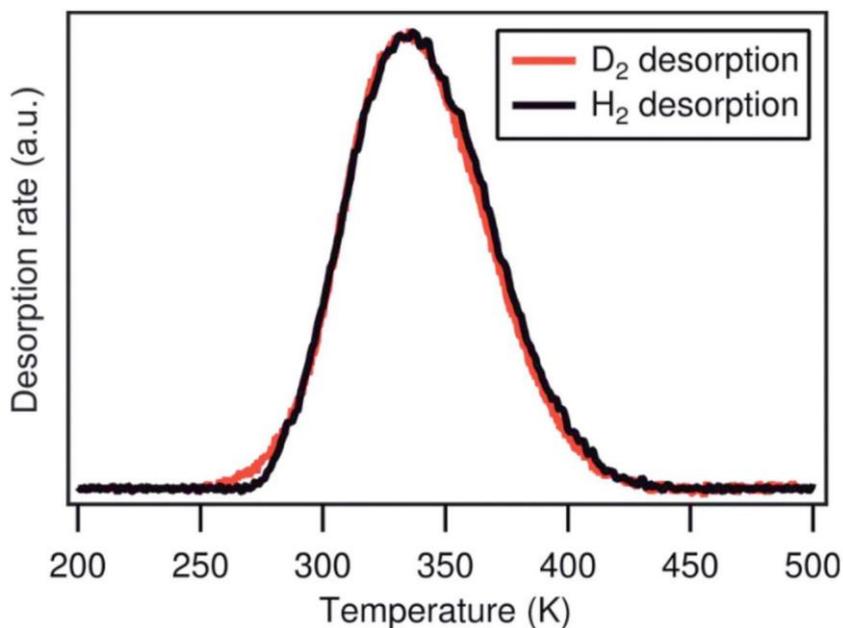


Fig. 1 H_2 and D_2 desorption from H_{ad} or D_{ad} -saturated $\text{Co}(0001)$ showing the identical desorption behaviour.

D_{ad}/D₂ occurs at the same temperature as the desorption of H₂, indicating that the desorption rate constant is not significantly affected by a kinetic isotope effect. The combination of a decreased collision frequency and a constant desorption rate constant translates to a higher free site concentration. In addition, both primary and secondary kinetic isotope effects will alter reaction rate constants of reactions that involve hydrogen. An example of the complexity that is introduced by replacing hydrogen by deuterium can be found in Fig. 2d in the article (DOI: 10.1039/C6FD00191B). The formation of CH₄ via CH₃ + H occurs at a significantly lower temperature than the formation of CH₃D via CH₃ + D. The formation of the more deuterated isotopologues, such as CD₄, occur at an even higher temperature.

1 M. Ojeda, A. Li, R. Nabar, A. U. Nilekar, M. Mavrikakis and E. Iglesia, *J. Phys. Chem. C*, 2010, 114, 19761–19770.

Michael Bowker addressed Eric van Steen and Kees-Jan Weststrate: In your case, halide is present with the adsorbates. Do you know if anyone has run experiments to look at the effect of halide in FT? I presume halide will be a poison for the reaction.

Eric van Steen responded: The effect of halides on the performance of FT-catalysts has been explored in particular by the Davis group due to the interest of converting syngas originating from biomass.

Over iron-based catalysts, Ma et al.¹ showed that the addition of up to 100 ppm of NaCl or KCl to the feed of the Fischer–Tropsch synthesis did not affect the activity or selectivity. The addition of hydro halide acids showed strong deactivation if the concentration increased to beyond 20 ppm (Ma et al.²), which was ascribed to competitive adsorption. In experiments in our lab, we showed that the addition of 50 ppm of chlorobutane resulted in complete, irreversible deactivation, which was ascribed to a phase transformation to FeOCl.

Over cobalt based catalysts, it has been observed that the addition of hydro halide acids increases the rate of deactivation (Gnanamani et al.³) proportionally to the amount present in the feed (in the range of 0.5–1 ppm), although the data is less clear than the data at higher levels for Fe-based catalysts. This has been ascribed to site blockage.

1 W. Ma, G. Jacobs, J. Kang, D. E. Sparks, M. K. Gnanamani, V. R. R. Pendyala, W. D. Shafer, R. A. Keogh, U. M. Graham, G. A. Thomas, B. H. Davis, *Catal. Today*, 2013, 215, 73–79.

2 W. Ma, G. Jacobs, G. A. Thomas, W. D. Shafer, D. E. Sparks, H. H. Hamdeh and B. H. Davis, *ACS Catal.*, 2015, 5, 3124–3136.

3 M. K. Gnanamani, V. R. R. Pendyala, G. Jacobs, D. E. Sparks, W. D. Shafer and B. H. Davis, *Catal. Lett.*, 2014, 144, 1127–1133.

Kees-Jan Weststrate responded: The influence of halogens has been studied on cobalt in the context of biomass derived synthesis gas by e.g. Rytter and coworkers¹ and on both Fe and Co catalysts by Davis and co-workers.^{2,3} In both cases, chlorine concentrations in the ppm range were used. Reported effects of halide addition range from very little effect¹ to mild poisoning.^{3,4} In the context of the paper where halogen-containing C₁ species serve as precursors for C₁H_x adsorbates, the main question is whether the halide product affects the C₁H_x chemistry. Various studies use the approach of halogenated precursor

compounds, and comparison with results from more complex but halogen-free precursors shows only small differences induced by the presence of halogen adsorbates alongside the C_1H_x moieties.^{5,6} In the discussion on this question, Prof. E. van Steen referred to the interesting study by van Barneveld and Ponec, where halogenated C_1 species were used in a fundamental study of the FTS mechanism on supported Co catalysts.⁷ They find that $CH_3Cl + H_2$ over Co catalysts only produced methane, whereas chain growth was found when CH_2Cl_2 and $CHCl_3$ were used instead.

- 1 Ø. Borg, N. Hammer, B. C. Enger, R. Myrstad, O. A. Lindvåg, S. Eri, T. H. Skagseth, E. Rytter, *J. Catal.*, 2011, 279, 163–173.
- 2 W. Ma, G. Jacobs, J. Kang, D. E. Sparks, M. K. Gnanamani, V. R. R. Pendyala, W. D. Shafer, R. A. Keogh, U. M. Graham, G. A. Thomas, B. H. Davis, *Catal. Today*, 2013, 215, 73–79.
- 3 M. K. Gnanamani, V. R. R. Pendyala, G. Jacobs, D. E. Sparks, W. D. Shafer and B. H. Davis, *Catal. Lett.*, 2014, 144, 1127–1133.
- 4 A. Paredes-Nunez, D. Lorito, Y. Schuurman, N. Guilhaume, F.C. Meunier, *J. Catal.*, 2015, 329, 229–236.
- 5 B. E. Bent, *Chem. Rev.*, 1996, 96, 1361–1390.
- 6 C. Chao-Ming and B. E. Bent, *Surf. Sci.*, 1992, 279, 79–88.
- 7 W. A. A. van Barneveld and V. Ponec, *J. Catal.*, 1984, 88, 382–387.

Paul Collier queried: In the Fischer–Tropsch process there is a lot of water present. This isn't treated in your model, would you expect this to change the conclusions?

Kees-Jan Weststrate replied: Water is indeed an important product in FTS and several studies show an impact on the catalyst activity and selectivity. A recent surface science study shows that water adsorbs weakly onto the cobalt surface and defects can induce dissociation.¹ Molecular water therefore most likely plays only a minor role due to its weak adsorption, and the main effect should be attributed to O and OH groups on the surface, in particular at step edge sites. As these sites play an important role in important steps in the FTS mechanism, such as CO dissociation² as well as dissociative adsorption of H_2 ,³ an increased concentration of O and/or OH will have a strong impact on FTS activity and selectivity.

- 1 L. Xu, Y. Ma, Y. Zhang, B. Chen, Z. Wu, Z. Jiang, W. Huang, *J. Phys. Chem. C*, 2010, 114, 17023–17029.
- 2 C. J. Weststrate, P. van Helden, J. van de Loosdrecht and J. W. Niemantsverdriet, *Surf. Sci.*, 2016, 648, 60–66.
- 3 P. van Helden, J. A. van den Berg and C. J. Weststrate, *ACS Catal.*, 2012, 2, 1097–1107.

James Hayward said: You show the monomers quickly dehydrogenating and forming acetylene on your surface. Do you see any evidence of the formation of any other C_2 products, or further chain growth products?

Kees-Jan Weststrate responded: In the spectroscopic studies that we did, we do not find any indication of products other than acetylene. If one looks at the stability diagram of C_2H_x species reported for example in ref. 1 and 2, one can see that acetylene is the most stable species and it is therefore the dominant product. Acetylene can react further by dehydrogenation to atomic carbon or by cyclo-polymerization to form benzene or graphene.^{1,2}

Further growth would, according to the alkyldiyne growth mechanism,^{3,4} require ethyldiyne species and CH species to co-exist on the surface. Formation of acetylene

consumes all CH present on the surface, and ethylidyne species do not form under the conditions used since they are less stable than acetylene for low surface coverages. When the surface coverage becomes high, other minor products might form as well. In ref. 4 and 5 we have recently shown that high surface coverage or a high coverage of CO co-adsorbates can lead to stabilization of ethylidyne species. The TPD experiment for the highly covered surface, shown in Fig. 2(b) in the article (DOI: 10.1039/C6FD00191B), shows a small hint for the formation of a minor C_2H_x product other than acetylene, characterized by a H_2 formation peak at around 360 K. It is tentatively attributed to the formation of a minor quantity of ethylidyne species, but further experiments would be needed to test this hypothesis.

- 1 Q. Y. Yang, A. D. Johnson, K. J. Maynard and S. T. Ceyer, *J. Am. Chem. Soc.*, 1989, 111, 8748–8749.
- 2 C. J. Weststrate, A. C. Kizilkaya, E. T. R. Rossen, M. W. G. M. Verhoeven, I. M. Ciobîcă, A. M. Saib and J. W. Niemantsverdriet, *J. Phys. Chem. C*, 2012, 116, 11575–11583.
- 3 C. J. Weststrate, I. M. Ciobîcă, A. M. Saib, D. J. Moodley and J. W. Niemantsverdriet, *Catal. Today*, 2014, 228, 106–112.
- 4 C. J. Weststrate, P. van Helden and J. W. Niemantsverdriet, *Catal. Today*, 2016, 275, 100–110.
- 5 C. J. Weststrate, I. M. Ciobîcă, J. van de Loosdrecht and J. W. Niemantsverdriet, *J. Phys. Chem. C*, 2016, 120, 29210–29224.

Emiel Hensen opened a general discussion of the paper by Pieter van Helden: It is very interesting to learn about microkinetics simulations starting from a multi-site model. The model also involves migration of species between different sites, for which an activation barrier is considered. The implicit assumption is that diffusion of the species and mixing over the sites is much faster than the exchange itself. Is this assumption reasonable? Did you check diffusion barriers and estimate their effect on the multisite microkinetic model?

Pieter van Helden answered: This is an important observation about the inter-site diffusion reactions. There are two types of diffusion in our model. The first is that on a surface site. These are described using the typical mean field assumptions as outlined in the paper, together with the inclusion of the constrained diffusion potential in the species entropy description (See the ESI of our paper for more details, DOI: 10.1039/C6FD00197A). We still need to check whether the on-site diffusion of species is significantly constrained in the presence of a high CO coverage. With a very few exceptions, surface diffusion processes typically have barriers significantly lower than those of the rate controlling surface processes at the relevant FT temperatures. Thus, as a first study of the FT multi-site mechanism, we accept the assumption as reasonable. The second type of diffusion is the inter-site diffusion, which have all been expressed as explicit reactions in the reaction network. Most of these barriers were calculated using DFT, while a small number were estimated based on the reaction energy and the terrace diffusion barriers. Since this second type of diffusion is an explicit reaction in the model, it was also included in the sensitivity analysis. At present, none of the inter-site diffusion reactions showed significant rate or selectivity control in any of the four considered scenarios. However, since we conclude that the high CO^* coverage is essential for the correct FT kinetic regime to exist, the inter-site diffusion of species in the presence of a high coverage of CO^* still needs to be assessed with DFT calculations.

Pieter van Helden commented: In our paper (DOI: 10.1039/C6FD00197A) we have employed sensitivity analysis to assess which steps and intermediates are rate and selectivity controlling. Although it does not play the biggest controlling role, the stability of the OH* species (especially on the step site) plays a smaller role in controlling the overall CO consumption rate. The direct steps of OH_x hydrogenation are therefore not rate limiting in the best fitting scenario (S4), but the thermodynamic stability of OH* seems to play a role. Thus the coverage of OH* on the step site is important for controlling the rate of CO consumption.

Moritz Wolf added: Our experimental results (DOI: 10.1039/C6FD00200E) lead to similar conclusions. Co-feeding water to synthesis gas (220 C, p_{H₂} ¼ 0.15 bar, p_{CO} ¼ 0.07 bar, p_{Ar} ¼ 0.78 bar, p_{H₂O} ¼ 0.02–1.45 bar) increased the magnetisation of a cobalt based catalyst when compared to the magnetisation during exposure to dry synthesis gas. This increase indicates the presence of OH* species on the cobalt surface, which are known to increase the magnetisation of surface cobalt atoms.¹ The conversion of CO decreased, while the amount of co-fed water was increased. Before oxidation of cobalt was observed, the conversion of CO was already less than 50% of the initial conversion at dry synthesis gas conditions, possibly due to blockage of active sites by adsorbed, water originated and thermodynamically stable OH* species. Hence, the presence of OH* on the cobalt surface does affect the CO consumption.

1 M. Claeys, M. E. Dry, E. van Steen, P. J. van Berge, S. Booyens, R. Crous, P. van Helden, J. Labuschagne, D. J. Moodley, and A. M. Saib, *ACS Catal.*, 2015, 5, 841–852.

Matthew Neurock asked: The model that you have developed involves 3 different sites that must all cooperate. This becomes difficult to understand. This may, in part, be due to the DFT results, which require 3 different environments. If I have this correct, you are assuming that CO dissociates via H-assistance at the step sites. The CH* species that form must then diffuse away from the step and onto the terrace sites. The CH* species would then diffuse across the CO-covered terraces until they find another CH* species that they can react with. This appears to be rather complicated. You indicate that C–O activation occurs more readily at the step sites. While this is true at low coverages, I don't think this would be the case at higher coverages as the more coordinatively-unsaturated Co sites here would bind the CO* or CH_x* and OH* intermediates much more strongly. As such, the higher coverages at these sites would significantly increase the barrier required for CO* to dissociate. In previously reported work on Ru,^{1,2} we showed that the CO binding energies and CO activation barriers significantly increase at the more coordinatively unsaturated step sites as well as edge and corner sites. I believe the DFT results that used in your simulations are those taken from low coverage DFT calculations. They may not be reflective of the barriers or the coverages present under actual FT conditions.

1 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.
2 D. Hibbitts, E. Dybeck, T. Lawlor, M. Neurock and E. Iglesia, *J. Catal.*, 2016, 337, 91–101.

Pieter van Helden replied: Our starting point in this work was the nanocrystal structure of FCC Co at a relevant size for the Fischer–Tropsch (FT) synthesis.¹ FCC Co nanocrystals at a representative size of 8 nm expose meaningful amounts of at

least five unique sites, of which two are terraces and the other three are defects/ step sites. These step sites are generally associated with the close-packed terrace. We approached the microkinetic model by not assuming upfront that any one of these sites favour any specific reactions. Furthermore, we allowed these sites to exchange surface intermediates, but did not assume upfront that they must cooperate. Thus, the interchange and cooperation we discuss in the paper emerge from the included kinetics at the considered conditions. As you note, the CH^* species is formed via a H-assisted CO dissociation on the step site in the final scenario of our model (although it does not need to be this specific mechanism). The results indicate that the CH^* species can indeed diffuse to the terrace surface. This happens with a free energy barrier of only 0.73 eV at 500 K. This is significantly lower than the overall FT process barrier. We agree that this process could indeed be affected by the coverage of other adsorbates at the step or terrace. Our results indicate that there is a high steady state coverage of both CO^* and OH^* at the step. This has to be explored further. As we note in our final conclusion, we demonstrated that the lateral interactions of reactive species with CO^* are of importance, especially in the role that CO^* could play in determining the kinetic parameters that need to be considered. As you rightly point out, CO dissociation process barriers have been shown to become higher in the presence of CO^* (although there are inverse cases for H-assisted pathways on Ni). From our models it is clear that if breaking the CO bond is rate limiting, chain growth will be severely limited due to the hydrogenation of monomers being more rapid than the production thereof. Thus, if the barrier of the dissociation process of CO^* at the step becomes too high, other possible pathways for splitting the CO bond could indeed be followed (maybe even similar to what was shown in Prof. Iglesia's lecture). However, such pathways should still not be rate limiting, and as such, are not the main concern in determining the controlling features of the FT reaction rate. The rate constant of the dissociation process could still be a controlling factor in the chain growth selectivity, by controlling the monomer concentration. As we conclude our discussion in the paper, we noted that the study of these steps under an appropriately high coverage of CO^* should be the focus of continued work in this regard.

It is also important to take note of the fact that this model does not include all three of the possible defect sites available on the FCC Co particle. Thus, other CO dissociation pathways on these sites should not be disregarded, but explored further.

Lastly, the DFT data for CO dissociation barriers we used in the model are obtained at a 0.25 ML coverage equivalent. However, if we compare these barriers to the most recent experimental work on direct CO dissociation on defect sites, these barriers seem to still be overestimated even by the low coverage DFT calculations. I refer you to section 3.3 of our paper (DOI: 10.1039/C6FD00197A) for a more extensive discussion.

I. P. van Helden, I. M. Cioba and R. L. J. Coetzer, *Catal. Today*, 2016, 261, 48–59.

Detlef Bahnemann remarked: Which are the active hydrogen species actually attacking carbon monoxide? Are these just hydrogen atoms or are reactive intermediates, such as hydride, also involved? Does the initial attack take place at the carbon atom or at the oxygen atom of the CO molecules?

Pieter van Helden responded: To my knowledge, there are no significant charge transfers happening in the dissociative hydrogen adsorption process on Co. Thus, the surface hydrogen that participates in the hydrogenation reactions are adsorbed atomic hydrogen. In the mechanisms of hydrogen assisted CO dissociation included in our model we considered both the attachment of H* on the C and the O atoms of adsorbed CO. On the two sites that can dissociate CO with any meaningful rate, the hydrogen assisted pathways seem to proceed preferably via attack on the C atom of the adsorbed CO, forming HCO*, which can subsequently dissociate into CH* + O*.

Enrique Iglesia asked: Let's address the experimental facts. Surfaces are saturated with chemisorbed CO at pressures between 5 kPa to 2 MPa as shown from infrared spectra; kinetic isotope effects and rate equations are consistent with H-assisted CO dissociation; DFT calculations indicate that direct CO dissociation is not feasible on low-index planes present on large particles that give highest turnover rates. Now you state that CO dissociation is fast and equilibrated based on isotopic exchange, even though the thermodynamics of such reactions would then lead to surfaces covered with C* and O* instead of CO*; this seems improbable. Have you considered that (i) such exchange may not require dissociation and that (ii) since you support the presence of two or more sites that one of those sites may be able to carry out the fast exchange without undergoing catalytic turnovers itself?

Pieter van Helden replied: The dissociation of the CO bond in FT is an important step, whether it is rate controlling or not. In our work on Co we claim that, given the outcomes of our microkinetic models, the CO scission process (via direct dissociation, HCO mediated or otherwise) should have a rate constant that could be considered to be "fast". This essentially should be understood as a fundamental rate constant higher than that of the rate limiting processes. That would mean that the CO dissociation step and its mechanisms is not such a key in understanding FT rates (although it might still play a role in the control of the selectivity profile). With this in mind "fast" CO dissociation does not in all cases lead to a surface covered with C* and O*. There are more factors at play in the steady state FT reaction network, such as availability of empty sites, coverages of other species, reversibility, rate of hydrogenation etc. For non-steady state results in the absence of hydrogen (not shown in the paper) C* is rapidly deposited on the surface, with an initial burst of CO₂ that forms, but this is also self-limiting as the C* quickly occupies most Co sites. This is not the scenario that is valid under the FT conditions studied here.

As is shown in Prof. Hensen's paper, the site he considered for Ru has a very high coverage of O* under steady state FT, due to the high rate constant of CO dissociation and the "slow" removal of O* to water. However, on Co the O* is rapidly hydrogenated to OH* on the step sites. These OH* species are quite stable on the B5 step sites. This stability ensures a moderately high coverage of OH* on the step sites, but still in line with the experimental SSITKA results (see our paper for more details). So in the case of Co FT, the surface is not rapidly covered with C* and O*, even if the CO dissociation is "fast". On Co nanoparticles there are a number of different exposed sites. Indeed the possibility exists that exchange could take place on one of the sites, without being part of the dominant FT

reaction network. However, we do not have any obvious indication from our micro-kinetics that would indicate this. In our model the most active CO scission process is directly linked to the rest of the FT reaction network while adsorbed CO* can easily migrate between the surface sites.

Matthew Neurock remarked: In the model you presented, you assume that the CH_x* species that form diffuse from the step edges and then across the terraces, where they can then find and react with another CH_x species. The diffusion of CH_x species through a dense adlayer of CO, however, would be difficult as it would occur via a random walk requiring the CH_x* species to diffuse through the formation of neighboring vacancies. These vacancies are random and as such, one would need to carry out a number of steps before the CH_x species would ever encounter one another. Even if the CH_x species are nearby, this would still require a number of diffusion steps for them to encounter one another. The mean-field microkinetic model assumes that diffusion is fast and would not address the stochastic nature of such processes.

Pieter van Helden replied: The mean-field model we employed in this work does assume that diffusion on a terrace site is significantly faster than the controlling steps and thus is described by the mean-field limit. The stochastic nature of such processes in the presence of species which modify the diffusion potentials through lateral interactions will attenuate the rate given by the mean-field model. In our model the diffusion of a species between dissimilar sites are explicitly included and will also be affected to an extent by the presence of a high coverage of CO*. For two CH* species to find one another and start chain growth on a terrace surface, they have to randomly traverse the terrace sites until they find each other, before they are hydrogenated to CH₄. The probability of this would depend on a number of factors: The effective diffusion barrier in the presence of CO*, the size of the terrace facet on the nanocrystal, the rate of CH* production and delivery to the surface facet. The effect of CO* on the barrier of diffusion of species is a valid concern and the detail thereof needs to be assessed with DFT calculations. However, it is important for all active species in the FT reaction in any case under high CO* coverage. The criterion for only two species to find each other on a terrace, without being the rate limiting step, would be a diffusion barrier that is more than 30 kJ mol⁻¹ lower than the overall barrier for the FT process (CO consumption rate). This would ensure that each CH* can undergo over a 1000 random hops in the time one CO is converted to a monomer. Furthermore, in the opening paper of the conference (DOI: 10.1039/C7FD00018A), the exibility of a high coverage CO* layer towards accommodating other intermediates was demonstrated. This would ensure that the CH* will not necessarily be fully blocked by the CO* overlayer. Typical supported Co FT catalysts have a distribution of Co nanocrystals in the nm range. An 8 nm FCC Co particle (as we used in our model) will expose a number of Co(111) terraces with an exposed diameter of about 16 to 20 sites (if no further overlayers of Co atoms are present). This would give a terrace area of about 400 sites that needs to be traversed by the CH* species. This is quite small and a random walk of over 100 steps would easily traverse all these sites. Furthermore, the rate constants for the process of producing CH* needs to be high enough that sufficient CH* is formed to promote chain growth over termination. Co SSITKA work¹ indicated that under steady state (even in methanation mode) the CH_x concentration is as high as 0.1 ML. Even if we

assume a lower coverage of 1%, this would still ensure that there are around four monomers on the typical 400 site terrace at steady state participating in the random walk. It would be quite feasible that they find each other. The overall rate of CO dissociation and production of monomers on the surface would control this concentration. In our model this would imply that the ratio of defect to terrace sites would be important.

If indeed the CO* would impede the diffusion of CH* over the terrace, this would mean that a diffusion gradient would develop from the defect site. One can imagine that the local higher concentration of monomers near the defect site would enhance the probability of coupling. Despite these arguments, this is a clear area for further fundamental study.

1 J. P. Den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen and K. P. de Jong, *J. Am. Chem. Soc.*, 2009, 131, 7197–7203.

Michael Claeys opened the discussion of the paper by Emiel Hensen: One of the major take home messages of your paper is that, based on your theoretical work, the chain growth probability with ruthenium goes through a maximum. Typically, in polymerization reactions, including the Fischer–Tropsch synthesis, a decrease of the chain growth probability is observed experimentally with an increase of reaction temperature. I am therefore surprised that you predict a decrease of alpha with decreasing temperature. This is particularly surprising seeing that ruthenium is known to produce a high molecular weight product ('polymethylene', see early work by Pichler¹) at low temperature conditions. Do you have, or are you aware of, any experimental evidence that supports your prediction that chain growth probabilities can indeed go through a maximum?

1 H. Pichler, B. Firnhaber, D. Kioussis and A. Dawallu, *Macromol. Chem. Phys.*, 1964, 70, 12–22.

Emiel Hensen answered: Indeed, we highlighted the occurrence of two Sabatier maxima, one with respect to CO consumption rate and one with respect to chain-growth probability. This is the outcome of the microkinetic model and the parameters obtained by DFT calculations. The latter values suffer of course from accuracy issues, which at least limit the absolute predictions of rates and also of the indicated maxima. So, the predicted maximum for chain-growth probability occurs at temperatures close to the FT conditions. We are not aware of an experimental gas-phase study showing that by lowering temperature the chain-growth probability goes down. However, we have published a paper on aqueous phase FTS,¹ in which we report that below 200 C we produce both long-chain hydrocarbons and long-chain oxygenates. Their alpha values are very different and for the long-chain oxygenates alpha goes through a maximum. Note the very low temperatures used, not sure if gas-phase studies have explored such low temperatures. We have also discussed the kinetics behind this behaviour. Of course, two types of products with different alpha values suggests two different sites – we have speculated about this in the indicated paper, but based on our current insights about what these two different sites might be, we may have to rethink the origin and then also the relation to the maximum predicted by the microkinetics simulations.

Matthew Neurock asked: You indicate that the barrier for CO to dissociate at the step site is low and as such, CO dissociation does not limit the rates. The references that were cited, however, were for calculations that were carried out on bare Ru surfaces at low coverage and have a barrier of $\sim 65 \text{ kJ mol}^{-1}$. As such, there are few repulsive interactions in the adlayer and the barriers to dissociate CO are low. The surfaces under working FT conditions, however, are covered in CO that may range from 0.67 ML to 1 ML of CO. You also note that the active surfaces are highly covered under reaction conditions. As such the barriers for CO dissociation would be higher. We have carried out calculations on large Ru particles and examined the barriers to dissociate CO on the terrace, B5-step sites and corner and edge sites. The barrier to dissociate CO on the step sites that you considered here at high CO coverages have an intrinsic barrier of at least 150 kJ mol^{-1} . The apparent barriers for CO dissociation at the step sites are significantly higher at 269 kJ mol^{-1} as they require the desorption of CO to create a vacancy to dissociate the CO.¹ If one considers the C* and O* that form at these sites, the barriers would be even higher. Even if one assumes that C* and O* are removed from these sites, they would be filled by CO* as CO is equilibrated. How do the simulation results change if you change the barriers that would be more reflective of the higher CO* coverages?

1 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, J. Am. Chem. Soc., 2013, 135, 6107–6121.

Emiel Hensen answered: The barrier energies as calculated by Neurock and co-workers are quite different from ours. The reason is that our model is a real B5 site as first coined by van Hardeveld et al.,¹ while Neurock² used a stepped site model (to be sure, and which is not a B5 site) on which CO dissociation is unfavorable. As already shown by us,³ the barrier at low CO coverage is 174 kJ mol^{-1} for such sites.

In your question, you correctly indicate that we have used a CO dissociation barrier at low coverage. The CO coverage is about $1/2$ ML. We have performed additional calculations up to $1/2$ ML coverage of CO. The CO dissociation barrier does not increase substantially; for instance, we find a CO dissociation barrier of 82 kJ mol^{-1} at $1/2$ ML. The underlying reason for this is that the topology of a step-edge site is such that significant lateral interactions are avoided up to a reasonable CO coverage (in our view lower than under real FT conditions). Furthermore, in your question you state that CO coverages range from 0.67 ML to 1 ML. We have not seen solid experimental evidence to support such high coverages. Our own SSITKA data show that under typical FT reaction conditions, the CO coverage is below 0.5 ML. This is in line with surface science experiments⁴ and coverages calculated by us and others.^{5,6} We have carried out some microkinetics simulations based on barriers reported by Neurock and Iglesia et al.,² including hydrogen-assisted elementary reaction steps. In our hands, this leads to very slow CO dissociation and consequently methane as the only hydrocarbon product. The fact that this should be the case can already be appreciated from the activation barriers (CO dissociation barrier is very high compared to other steps, which is

inconsistent with conditions for chain growth). The apparent activation energy in these simulations is very high ($> 150 \text{ kJ mol}^{-1}$), which is inconsistent with the experiment. Our microkinetic simulations, on the other hand, produce activation energies below 100 kJ mol^{-1} , consistent with experimental data being in the $80\text{--}120 \text{ kJ mol}^{-1}$ range.

- 1 R. van Hardeveld and A. van Montfoort, *Surf. Science*, 1966, 4, 396–430.
- 2 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.
- 3 X.-Y. Quek, I. A. W. Filot, R. Pestman, R. A. van Santel, V. Petkov and E. J. M. Hensen, *Chem. Commun.*, 2014, 50, 6005–6008.
- 4 G. A. Beitel, A. Laskov, H. Oosterbeek and E. W. Kuipers, *J. Phys. Chem.*, 1996, 100, 12494–12502.
- 5 G. T. K. K. Gunasooriya, A. P. van Bavel, H. P. C. E. Kuipers and M. Saeys, *Surf. Sci.*, 2015, 642, L6–L10.
- 6 M. Zhuo, A. Borgna and M. Saeys, *J. Catal.*, 2013, 297, 217–226.

Kees-Jan Weststrate enquired: One of the main themes in the various presentations during the conference is that the CO concentration under reaction conditions is expected to be high, and that this should be taken into account when considering the surface chemistry of FTS. It is for example an essential ingredient of the studies by the groups of Iglesia et al.¹ and Saeys et al.² on Ru and Co catalysts, respectively. In Fig. 4 of your article (DOI: 10.1039/C6FD00205F) you show that the CO coverage at 600 K is only 0.03 ML, whereas the vacancy concentration is 0.14 ML and the remaining sites are covered by O, C and H. With an impingement rate of CO molecules in the order of $5 \cdot 10^8$ ($\frac{1}{46.7}$ bar at 600 K) the barrier for desorption (with an assumed pre-factor of $1 \cdot 10^{15}$) then has to be around 60 kJ mol^{-1} to arrive at a q_{CO}/q^* of 0.22. This seems like a very low adsorption energy for CO on Ru. In your presentation you mentioned that the CO concentration at step sites is low because of the high reactivity of these sites. But the reaction that consumes CO can only significantly impact the value of q_{CO}/q^* produced by the adsorption–desorption equilibrium when its rate is in the same order of magnitude as the adsorption and desorption processes, that is, 10^8 s^{-1} .

The question is twofold: 1(a) why are there so many free sites at 600 K (Fig. 4, DOI: 10.1039/C6FD00205F) despite the presence of 6.7 bar of CO? 1(b) Does the statement that the CO concentration at the step edges is low because of the high reactivity of step sites imply that the CO consumption reaction there is in the order of 10^8 or does it mean something else?

2 In the article you mention that the rates of the elementary reaction steps that convert the alkyne coupling product ($\text{HC-CR} / \text{C-CH}_2\text{R}$), a process which requires two hydrogenation steps and one dehydrogenation step, strongly affect the selectivity of the FTS reaction. In our experimental study we found that the conversion of acetylene to ethylidyne ($\text{C}_2\text{H}_2 + \text{H} / \text{CCH}_3$) occurs with surprising ease on Co(0001) when CO is present on the surface as well.³ Due to the abundance of CO, the free site concentration is expected to be low, yet the reaction proceeds at around 250 K already. With such facile reaction kinetics, how can the kinetics of these steps involved still be so important at typical reaction temperatures of 500 K?

- 1 D. Hibbitts, E. Dybeck, T. Lawlor, M. Neurock and E. Iglesia, *J. Catal.*, 2016, 337, 91–101.
- 2 M. Zhuo, A. Borgna and M. Saeys, *J. Catal.*, 2013, 297, 217–226.
- 3 C. J. Weststrate, P. van Helden and J. W. Niemantsverdriet, *Catal. Today*, 2016, 275, 100–110.

Emiel Hensen replied: Let's start off by discussing your assumptions. We calculate, including lateral interactions, an adsorption energy of around 80 kJ mol^{-1} at 600 K. Combined with an activation energy of 65 kJ mol^{-1} for CO dissociation, this results in a situation where the CO desorption rate matches the CO dissociation rate. Hence, one can no longer apply the quasi-equilibrium assumption.

Answer to question 1: in your question you refer to high CO coverage as suggested by several papers. Let me first comment on these references.

As to ref. 1 in your question, Iglesia et al. use a very high coverage of CO in their discussion, higher than one ML. In the mentioned paper, a value of 1.04 ML is used, which is attributed to full coverage of planar surface atoms with an unlikely 1 CO per surface metal atom assumption augmented by coverage of steps and corners with dicarbonyls. There is no solid experimental evidence presented for such high coverage. As to the references mentioned in the Iglesia paper to support this high coverage, it can only be concluded that CO is the most common adsorbate.

Ref. 4 of this paper¹ discusses SSITKA data, showing that the surface is mainly covered by CO, some C₁ species and a very small amount of growing chains. The absolute coverage of CO is not calculated as the dispersion is unknown.

1 C. A. Mims and L. E. McCandish, *J. Phys. Chem.*, 1987, 91, 929–937.

Ref. 5–7 of this paper^{2–4} use just the fitting of L–H rate equations that could be interpreted as CO being the most abundant surface species. Of course, kinetics do not prove a mechanism.

2 R. S. Dixit and L. L. Tavlarides, *Ind. Eng. Chem. Process Des. Dev.*, 1983, 22, 1–9.

3 M. Ojeda, R. Nabar, A. U. Nikelar, A. Ishikawa, M. Mavrikakis and E. Iglesia, *J. Catal.*, 2010, 272, 287–297.

4 I. C. Yates and C. N. Satterfield, *Energy Fuels*, 1991, 5, 168–173.

Ref. 8 of this paper⁵ presents IR data that confirms the presence of carbonyls, but without quantification. Quantification is only done using theoretical calculations. As outlined in our answers to Prof. Neurock, we also contend that the di- and tri-carbonyl bands reported for supported Ru nanoparticles upon CO adsorption are in fact positively charged Ru species due to partial oxidation. As to ref. 2, Saeys and co-workers found that at Fischer–Tropsch conditions (at 6

bar) the maximum coverage is $\frac{1}{3}$ ML. Higher coverages might theoretically be possible (up to a maximum of 0.58 ML) but are unstable. So there will always be abundant free sites. We conclude that there is no convincing evidence for a very high CO coverage during FTS. Of course, when such an assumption is made, there is a need for unusual mechanisms, as explored by the group of Prof. Neurock, that should explain Fischer–Tropsch synthesis on a densely CO-covered surface.

5 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.

Our own SSITKA data show that under typical FT reaction conditions, the CO coverage is below 0.5 ML. This is in line with surface science experiments and our own and others' DFT calculations (coverage).^{6,7} Also, we have never found indications for dicarbonyls present when Co nanoparticles are exposed to CO (nor did the spectra presented by Prof. Iglesia in his lecture provide evidence for such CO species on a Co nanoparticle catalyst, in which he also mentioned that the surface

is already saturated at relatively low CO pressure). We argue that all this is not at odds with our microkinetic simulations as SSITKA will measure all reversibly adsorbed CO species and reversibly dissociated CO for that matter. Our micro-kinetic model pertains to step-edge sites, which on a real nanoparticle are present as a minority site together with many more low reactive sites (different terraces, etc.), where steady-state coverage will be much higher. To take this properly into account, a multi-site model is needed, which brings its own challenges but seems doable (see the work of Dr van Helden, DOI: 10.1039/C6FD00197A).

Further transient data emphasize that the rate of desorption is of the same order as the rate of CO dissociation. Accordingly, we expect that the rate of adsorption is also of the same order.

Question 2: Firstly, we would like to point out that we looked at a Ru step and not at a Co surface. Furthermore, we did not study the equilibrium of the reaction but the kinetics and thus selectivity. The experiments⁸ you are referring to emphasize the easy conversion of acetylene to ethylidene. In the same paper, experiments are cited that show that CH to CH coupling also runs at 250 K. In the paper these two are added together to describe the chain growth. It does, however, not explain why a temperature 500 K is needed for the Fischer–Tropsch reaction. We calculate that on Ru(11–21):

The pathway HC–CH / HC–CH₂ / C–CH₂ / C–CH₃ has an overall barrier of 83 kJ mol⁻¹ (21 kJ mol⁻¹ from HC–CH₂) and results in a chain fragment.

The pathway HC–CH / HC–CH₂ / H₂C–CH₂ has the same overall barrier of 83 kJ mol⁻¹ (45 kJ mol⁻¹ from HC–CH₂) and results in products that can desorb. As shown in the paper, these energies explain well that a temperature of 500 K is needed for the Fischer–Tropsch reaction to occur.

6 G. T. K. K. Gunasooriya, A. P. van Bavel, H. P. C. E. Kuipers and M. Saeys, *Surf. Sci.*, 2015, 642, L6– L10.

7 M. Zhuo, A. Borgna and M. Saeys, *J. Catal.*, 2013, 297, 217–226.

8 C. J. Weststrate, P. van Helden and J. W. Niemantsverdriet, *Catal. Today*, 2016, 275, 100– 110.

Michael Bowker commented: In your CO scrambling experiments why doesn't the reaction poison itself with carbon via the Boudouard reaction? I find it surprising that C isn't formed in this way because I would imagine the CO oxidation reaction is relatively easy once some CO is dissociated.

Emiel Hensen replied: During the CO scrambling reaction, CO₂ is produced, but this reaction stops relatively quickly. When the surface is exposed to ¹²C¹⁶O only, then obviously CO₂ is also observed and its production stops soon after CO exposure. It means that during CO exposure, C atoms remain at the surface. Titration of these C atoms by H₂ is possible and shows that with increasing exposure time to CO, the C/CO(surface) increases but never becomes very high. Despite this laydown of C atoms, the surface is still able to reversibly dissociate CO. Moreover, Fischer–Tropsch rates before and after carbon laydown are very similar, even with a significant part of the carbon remaining there (as it can only be removed by hydrogenation above 300 °C).

Our explanation is as follows. CO dissociates reversibly on a minority site (we presume these are step-edges). Part of the C and O atoms migrate to the terraces, which are more ubiquitous and are covered with spectator CO. CO reacts with O to

form CO₂, but the C atoms, in the absence of H, remain and start blocking the terraces such that CO₂ production ceases. The nature of the C overlayer is unclear, although, as I said, part of it requires reduction above 300 C to be removed, suggestive of a graphene-like layer being formed.

Pieter van Helden asked: It seems that oxygen species are quite stable on the sites of both Co and Ru. In our Co microkinetic model, oxygen is most stable as OH* on the step site. In the scenario where we find the best fit with experiments (S4), the OH* covers about half the step sites. In your Ru model, on the single step site the O* coverage is quite dominant under FT conditions. In our Co case, hydrogenation of O* to OH* is quite rapid and therefore you would not expect a high probability of forming CO₂ via the CO* + O* reaction on that site. This is indeed what you see experimentally in Fischer–Tropsch, that CO₂ selectivities are in the single percentage points under relevant conditions. However, a significant amount of CO₂ is still produced in our Co model, predominantly at the Site-B/Co(100).

Emiel Hensen answered: The kinetic data show that O hydrogenation is more difficult on Ru than on Co. This explains the difference in our data. We have used a single-site model so we do not include a CO₂ formation pathway on a low-reactive surface. We would argue that on a low-reactive surface the CO coverage is high so that any O migrating there will be removed as CO₂. An important aspect/ challenge in simulating multiple sites with migration might be to correctly describe diffusion/mixing rates.

Enrique Iglesia enquired: Given the very high rates of reactions of CO* with O* and your proposal that CO dissociation is fast and equilibrated, how does one avoid stranding C* behind and causing rates to decrease precipitously with time? Even a very infrequent O*–CO* event would cause almost instantaneous high coverages of C* in light of your very high turnover rates for exchange both with and without H₂ present. How do you explain the absence of deactivation and the CO₂ formed via Boudouard reactions as the predominant product?

Emiel Hensen answered: Recent kinetic experiments involving isotopic CO scrambling in the presence of H₂ show that CO dissociation is reversible, but not totally equilibrated. Changing the scrambling measurements from pulsing mode to continuous flow mode indeed leads to build up of C species and deactivation. A key point is that most of the activity already disappears by formation of about 10– 20% of the surface sites, suggesting that CO dissociation only occurs at a minority site. This C lay-down is suppressed in the presence of hydrogen, leading to formation of CH₄ and other hydrocarbons and H₂O (more easy to form H₂O than CO₂).

Linda Jewell communicated: One of the things that you said is that chain growth is reversible under FT conditions. This suggests that equilibrium can be established between alkanes of different lengths, but in general the distribution obtained is not an equilibrium distribution.

If chain growth is reversible, why do you think alkanes are not at equilibrium under FT conditions?

Emiel Hensen communicated in response: The fact that chain growth is reversible does not mean it is equilibrated. The chain length distribution is determined by the kinetics in this case, not by equilibrium. At low temperatures, there are few vacancies so that the forward reaction that propagates the chain is much faster than the reverse decoupling. Hence, long chains are formed. At high temperatures, there are vacancies so that the rate of decoupling is much higher than the rate of chain growth and mostly methane is obtained.

Hans Niemantsverdriet opened the general discussion and addressed Emiel Hensen, Pieter van Helden and Enrique Iglesia: Comparing the lecture of Prof. Iglesia with that of Prof. Hensen and Dr van Helden, we interestingly see the difference in approaches between the conventional 'one-site does it all' Lang-muir-Hinshelwood approach and that of micro-kinetic modelling, where you allow for the cooperation of step sites with terrace sites. Prof. Iglesia cited the first order hydrogen dependence in the context of his LH rate expression over a range of different conditions as compelling evidence that hydrogen must be involved in the rate determining step, namely CO dissociation. Dr van Helden and Prof. Hensen, in agreement with our own work,¹ do not consider CO dissociation as rate determining. In the latter view, the first order dependence in $p(\text{H}_2)$ could well be due to the removal of O-atoms from the surface, or from other hydrogenation steps in the reaction sequence. However, the fact that many steps in the hydro-carbon surface chemistry can occur at room temperature or below,^{1,2} points to O-removal, which indeed has a high barrier.³ What is your opinion?

Secondly, is it possible to derive an overall rate equation from your micro-kinetic modelling equivalent to the LH expression, so that a direct comparison might be possible?

1 C. J. Weststrate, P. van Helden and J. W. Niemantsverdriet, *Catal. Today*, 2016, 275, 100–110.

2 C. J. Weststrate, I. M. Ciobancu, A. M. Saib, D. J. Moodley, J. W. Niemantsverdriet, *Catal. Today*, 2014, 228, 106–112.

3 C. J. Weststrate, J. van de Loosdrecht and J. W. Niemantsverdriet, *J. Catal.*, 2016, 342, 1–16.

Emiel Hensen responded: Let us answer the second question of Prof. Niemantsverdriet first – with microkinetic modeling it is very easy to compute CO conversion rates as a function of temperature and partial pressure and then fit them with LH equations, just like one would do with experimental data. We have not done so for our predicted Ru data, but power rate law fits of these data produce reaction orders with respect to CO and H_2 of 0.2 and ~ 1 in good agreement with the LH-type equation shown by Prof. Iglesia. Then, a degree of rate control analysis for the Ru-catalyzed FT reaction shows that CO consumption rate is completely controlled by O removal. Note that this pertains to Ru (see our *Angewandte Chemie* paper).¹ Thus, the observed kinetic parameters do not prove CO dissociation is rate limiting. Prof. Iglesia assumes that CO dissociation is rate limiting (probably he has some indications for this, different from the kinetics). If the reaction order in H_2 is 1 then indeed this implies that CO dissociation – the first step in the kinetic scheme – should be H-assisted and one would have to introduce a HCOH or H_2CO species, for which the C–O bond cleavage is then rate limiting.

In the Ru simulations, we find that O removal is rate limiting. This requires one or two H atoms, which can explain the reaction order in H₂ being 1. In the Ru case, the rate control of O removal is high so that one could say there is one rate limiting step.

Based on our microkinetic modeling of Co, we predict that both O removal and CO dissociation are rate controlling – this makes the use of LH rate equations cumbersome as there is not one rate limiting step. Note that these predictions are in line with the works mentioned by Prof. Niemantsverdriet. Although the CH_x (de)hydrogenation steps are indeed facile (e.g. accessible at room temperature or below) under FT and methanation conditions, they are not fast as coverages are high or the surface gets depleted in H, respectively. Prof. Iglesia raised a solid point that if O removal is rate limiting, the surface should be full with O – experimentally the surface is observed to be full with CO. Here is the basis of our very different view: to explain this we require at least two sites, and these are in our opinion step-edges for low-barrier CO dissociation, where nearly all the FT chemistry takes place, and terraces that contain spectator CO (and produce CO₂ with O atoms spilling over from the step-edges to the terraces).

I. A. W. Filot, R. A. van Santen and E. J. M. Hensen, *Angew. Chem., Int. Ed.*, 2014, 53, 12746–12750.

Pieter van Helden added: I am of the opinion that it is very difficult to directly relate the reaction orders of a multi-step surface reaction only to one single rate limiting step. From our sensitivity analysis, it is clear that there are a number of rate controlling features at typical Fischer–Tropsch conditions. However, we showed in our contribution that both the concentration of H* and the partial hydrogenation of the CH₃* species on the step site plays an important rate controlling role. This would indeed point to a positive dependence of the rate on the pressure of hydrogen. In our paper (DOI: 10.1039/C6FD00197A) we argue that the CO scission process cannot be rate limiting and it is therefore my opinion that the first order in hydrogen relates to a hydrogenation step. It is also worth noting that both the two published macrokinetic models, which describe the experimental pressure-rate relationship, the best overall (referred to in our paper, DOI: 10.1039/C6FD00197A) has the pressure of hydrogen expressed to the power 0.75. It is interesting to note that in the assumed mechanisms underlying the derivation of these models, one employed direct CO dissociation and the other used a hydrogen assisted CO dissociation. In both cases they resulted in the same order in hydrogen (although the CO orders differ somewhat). Regarding the second part of the question: I believe it is possible to derive an overall rate equation from our microkinetic modelling work. One way is to take the proposed reaction network, rate-limiting steps and dominant surface species, and derive a mechanistically based macrokinetic model. In my experience this could become a difficult task if you use two active sites explicitly in your model, resulting in having to solve a high order polynomial to be able to ensure you have a closed form equation. Thus, although it is surely possible, you would need some smart mathematics to keep it simple. Thus far, we have not put significant effort into this in our team.

Enrique Iglesia replied: The kinetic relevance of the oxygen removal step would not be consistent with the well-demonstrated presence of CO as the predominant

chemisorbed species during catalysis, while quasi-equilibrated CO dissociation would lead to the predominance of C* and O* as the adsorbed species (instead of CO* in the molecular form). Of course, at steady-state, carbon removal must occur at the same rate as oxygen removal, thus the kinetic relevance of one is not possible without that of the other one, returning us once again to the earlier proposals of H-addition to C* and the subsequent step as the sole kinetically relevant ones. A first-order dependence on H* would require equilibration between O* and H* and a kinetically relevant addition of the second H* to OH*; this is inconsistent with the very fact of isotopic exchange between H₂O and D₂O (and between both and H₂ or D₂) during the practical conditions of Fischer–Tropsch catalysis. Such proposals would also fail to account for the measured kinetic isotope effects and for theoretical assessments that demonstrate the high barriers for CO dissociation on low-index planes, on corners and edges, and on all except possibly unique step sites, the prevalence of which would be difficult to envision to be the same on large particles of varying size, which show similar turnover rates at the conditions of the Fischer–Tropsch synthesis.

Pieter van Helden addressed Emiel Hensen, Kees-Jan Weststrate and Matthew Neurock: Regarding the coverage of CO at steady-state Fischer–Tropsch (FT) conditions, it is important to note the typical rate of desorption of CO at these temperatures. The pre-exponential factor of desorption and the desorption heats are such that at FT conditions the temperature is above the desorption temperature of CO. Thus, there will be a rapid exchange of CO on the surface with that of the gas phase. This rapid exchange will create transient, short-lived empty sites on the surface. The adsorbed CO layer on the surface can therefore not be considered to be statically blocking the sites. It has been shown through in-house computational work and surface science experiments, as well as previous well-known surface science work (referred to in our paper, DOI: 10.1039/C6FD00197A) that the CO surface coverage on the close packed Co surface saturates to a value lower than a monolayer of Co. This value is noted to be around 0.67 ML. This value is not as high as was noted by Prof. Iglesia in his paper (DOI: 10.1039/C7FD00018A). At such a saturation coverage there will be some sites still available for the smaller adsorbates. Once the surface reaches this saturation coverage, it becomes difficult to push more CO onto the surface due to the strong repulsive lateral interactions, which negate the effect of CO binding to the surface. It is these lateral interactions of CO with other adsorbates that pushes up the energies of these adsorbates and transition states into a different kinetic regime.

Emiel Hensen replied: Thank you for this comment. Our calculations and those of Mark Saeys¹ emphasize that the (0001) surface saturates at 0.67 ML. Also, in response to an earlier question from Dr Weststrate, I would like to comment on fast adsorption/desorption. Indeed, using the usual considerations we find that CO adsorption/desorption rates must be fast compared to CO consumption. However, a simple transient experiment in the spirit of Prof. Kruse² tells us something different. If we switch the CO/H₂ feed for Co/SiO₂ to a H₂ only feed, all the CO on the surface will be consumed and form hydrocarbons – CO does not desorb. We determined CO coverages (determined by SSITKA, range 0.1–0.4) as a function of the partial pressure of CO and then carried out the transient experiment (switched CO/H₂ to H₂). We counted the carbon atoms coming out in

the form of hydrocarbons and they matched the total amount of CO on the surface. Thus, the rate of desorption is certainly not fast compared to the rate of CO dissociation. It is an important experimental observation, which is inconsistent with the simple adsorption/desorption kinetics we assume in our modeling and in our considerations.

1 M. Zhuo, A. Borgna and M. Saeys, *J. Catal.*, 2013, 297, 217–226.

2 J. Schweicher, A. Bundhoo and N. Kruse, *J. Am. Chem. Soc.*, 2012, 134, 16135–16138.

Kees-Jan Weststrate added: In a recent review we have summarized experimental findings about CO adsorption on cobalt surfaces, in particular the close-

packed surface.¹ We find that at 90 K a coverage of 0.83 ML ($\frac{6}{7}$) can be reached when using CO pressures of $1 \cdot 10^3$ mbar. At lower pressures a coverage of 0.67 ML ($\frac{2}{3}$) can be reached. When we extrapolate our data measured in pressures up to 10^3 mbar CO to FTS pressures and temperatures, we find that those two states are not populated, and instead a coverage of around 0.5 ML is found, associated with an adsorption energy of around 90 kJ mol⁻¹.² This prediction matches the SSITKA results reported by Den Breejen et al.; they use 55 mbar CO in 550 mbar CO at 483 K and report a CO coverage of 0.43 on the larger particles which exhibit good FTS performance.³ By exploring the adsorption–desorption equilibrium we can get some insight into how adsorption energies translate to coverage, and by looking at the rate constants we can get an idea about the dynamics of the system.⁴ When assuming a pre-factor for desorption of $1 \cdot 10^{15}$ and $T \approx 500$ K, an adsorption energy of 67 kJ mol⁻¹ would produce a desorption rate constant equal to the influx of CO molecules at 1 bar, approx. $1 \cdot 10^8$ per surface atom per second. Vice-versa, for the surface state corresponding to an adsorption energy of 90 kJ mol⁻¹, 99.6% would be occupied. Yet, the desorption rate constant at this point would still be $4 \cdot 10^5$ with an average residence time per CO molecule of $2.5 \cdot 10^6$ s. A state with an adsorption energy of 100 kJ mol⁻¹ would be 99.97% occupied, yet the rate constant would still be $3 \cdot 10^4$, with a residence time of $3.3 \cdot 10^5$ s. At 120 kJ mol⁻¹ we obtain a residence time of $3.3 \cdot 10^3$ s. To summarize, CO coverage on cobalt is expected to be around 0.5 ML, a notion that is supported by SSITKA data. The situation is dynamic, with random appearance and disappearance of vacant sites on the millisecond timescale or faster.

1 C. J. Weststrate, J. van de Loosdrecht and J. W. Niemantsverdriet, *J. Catal.*, 2016, 342, 1–16. 2 H. Papp, *Surf. Sci.*, 1983, 129, 205–218.

3 J. P. Den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen and K. P. de Jong, *J. Am. Chem. Soc.*, 2009, 131, 7197–7203.

4 C. J. Weststrate, P. van Helden and J. W. Niemantsverdriet, *Catal. Today*, 2016, 275, 100–110.

Matthew Neurock answered: High pressure CO adsorption surface science studies carried out on Ru(0001) show that the CO coverage monotonically increases from 0.67 ML at typical UHV conditions (10^8 torr) to ~0.9 ML of CO at 0.1 torr.¹ This study, which was carried out at CO pressures of up to 0.1 torr is still 3–4 orders of magnitude lower than the 1–10 atm CO pressures used for FTS. At the high pressure conditions and FTS temperatures, CO is quasi-equilibrated on the surface.

CO readily desorbs at these temperatures but is rapidly replaced as a result of the high gas phase pressures. The rate of CO adsorption is significantly higher than the rates of reaction. The high saturation coverages on CO are fully consistent with reported in situ infrared analyses,^{2,3} isotopic labeling studies⁴ and kinetic studies⁵ that indicate that surfaces are fully covered at the conditions of Fischer–Tropsch. The CO saturation coverage on metal particles is also significantly higher than that on single crystal surfaces, as the metal particles expand radially to relieve the stress induced by the repulsive interactions between the oxygen atoms on neighboring CO molecules, thus creating more curvature along the surface and allowing the CO molecules to point outward and away from one-another. Single crystal surfaces cannot accommodate the high stress that would result from the repulsive interactions. As such, single crystal surfaces either saturate at lower coverages (0.67–0.9 ML) or reconstruct. Theoretical and experimental results for Ru particles show CO coverages > 1 ML.^{2,6}

1 D.E. Starr and H. Bluhm, *Surf. Science*, 2013, 608, 241–248.

2 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.

3 P. Winslow and A.T. Bell, *J. Catal.*, 1984, 86, 158–172.

4 C.A. Mims and L.E. McCandlish, *J. Phys. Chem.*, 1987, 91, 929–937.

5 M. Ojeda, R. Nabar, A.U. Nilekar, A. Ishikawa, M. Mavrikakis and E. Iglesia, *J. Catal.*, 2010, 272, 287–297.

6 D. Hibbitts, E. Dybeck, T. Lawlor, M. Neurock and E. Iglesia, *J. Catal.*, 2016, 337, 91–101.

Matthew Neurock commented: Many appear to agree that under FT conditions the metal Ru and Co surfaces have high CO coverages. There is some debate, however, as to what the actual coverages are. Single crystal surface science studies indicate that the coverages on Co(0001) and Ru(0001) surfaces are ~0.67 ML. We calculate very similar saturation coverages to those from experiments on Co(0001) and Ru(0001) surfaces (~0.67 ML).¹ On particles, however, the surface coverages are significantly higher as the surfaces of the metal particles expand. This is consistent with EXAFS data for CO on particles. In addition, the CO molecules can fan away from one another to relieve some of the steric repulsion from the CO groups. Single crystal surfaces, however, are constrained laterally and as such cannot relieve themselves from the strain that results from the repulsion from the repulsive CO* interactions. At high enough coverages, however, they release the strain by reconstruction. Our previous calculations indicate that one can go up to 1.05 ML on 201 atom¹ and 586 atom Ru particles.² The Ru particles expand radially to allow for higher packing. In addition, the coordinatively unsaturated edge and corner Ru atoms will bind 2 and 3 CO molecules, respectively, to complete their coordination sphere. This is consistent with experimental, kinetic and in situ IR spectroscopic studies, which indicate coverages > 1 ML and the presence of di- and tri- carbonyls.¹

1 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.

2 D. Hibbitts, E. Dybeck, T. Lawlor, M. Neurock and E. Iglesia, *J. Catal.*, 2016, 337, 91–101.

Kees-Jan Weststrate answered: Before discussing CO on ruthenium nano-particles, it is important to realize that cobalt and ruthenium are different in various ways. Fig. 1 shows a comparison of the TPD spectra for CO from Co(0001) and Ru(0001), respectively (obtained in the same vacuum system, with the same heating rate, etc.) It is clear that, although in both cases the total coverage is 0.67 ML, the

desorption temperature found on Ru is much higher. This higher adsorption energy on Ru would translate to a higher saturation coverage at reaction conditions for Ru compared to Co.¹ On the close-packed Ru, a CO coverage of up to 0.9 ML was reported at room temperature² for pCO $\frac{1}{4}$ 1 Torr, but it is not obvious that this state can be reached at 500 K, even when the pressure is 4 orders of magnitude higher. Secondly, because of the 10% smaller diameter of cobalt atoms, the situation regarding lateral interactions is different. This can be seen in infrared experiments: on Ru(0001) only the top sites are occupied up to a coverage of 0.67 ML, the low pressure saturation point.³ Instead, on Co(0001) we find top-only up to 0.33 ML, top-hollow between 0.33–0.5 ML, bridge-top between 0.5–0.67 ML and hollow-top between 0.67–0.83 ML, i.e. much more complex.¹ Finally, Co nanoparticles in the relevant regime for FTS often have the bulk fcc structure⁴ and thus expose predominantly (111) surfaces, with (100) facets being second most abundant.⁵ Instead, Ru nanoparticles adopt a hcp structure. The lower symmetry of the hcp unit cell implies that spherical particles can only expose the close-packed surface on two opposing faces, and the other surfaces must have a different, more open structure. As a consequence, the close-packed surface accounts for only a small part of the surface, and a large quantity of more open surfaces, such as (10–10) and (11–20) are exposed.^{6–8} It is therefore not obvious at all that the small (2.5 nm), cubo-octahedral particles used in ref. 9,10, which are fully terminated by close-packed surfaces, are representative of 7 nm hcp-Ru catalyst particles. The presence of significant quantities of surface structures, such as (10–10) and (11–20), has important consequences: CO coverages up to 1.25 ML have been reported for the (10–10) surface,¹¹ which would translate to a global coverage >0.67 ML in a Ru nanoparticle. In addition, surfaces such as (11–20) will be exposed, which have been found to be very active for CO dissociation.¹² To add to the complexity, some of the ordered adsorbate structures found for high coverages on extended single crystal surfaces might not form on the small terraces exposed by nanoparticles, see e.g. the discussion in ref. 13. Thus, surface science reveals the complexity of CO adsorption and the pressure–coverage relation even on well-defined cobalt and ruthenium surfaces. On small nanoparticles the convex surface and lattice expansion can serve to relax repulsive adsorbate interactions, thereby stabilizing higher surface coverages. Calculations in ref. 9,10 suggest that such relaxation indeed takes place for small clusters, but whether this extends to 7 nm particles is not yet clear.

1 C. J. Weststrate, J. van de Loosdrecht and J. W. Niemantsverdriet, *J. Catal.*, 2016, 342, 1–16. 2 D.E. Starr and H. Bluhm, *Surf. Science*, 2013, 608, 241–248.

3 H. Pfnur, D. Menzel, F. M. Hoffmann, A. Ortega and A. M. Bradshaw, *Surf. Sci.*, 1980, 93, 431–452.

4 O. Kitakami, H. Sato, Y. Shimada, F. Sato and M. Tanaka, *Phys. Rev. B*, 1997, 56, 13849. 5 P. van Helden, I. M. Cioba and R. L. J Coetzer, *Catal. Today*, 2016, 261, 48–59.

6 R. M. Nielsen, S. Murphy, C. Strebler, M. Johansson, I. Chorkendorff and J. H. Nielsen, *J. Nanopart. Res.*, 2010, 12, 1249–1262.

7 J. Gavnholt and J. Schiøtz, *Phys. Rev. B*, 2008, 77, 035404.

8 X.-Y. Quek, I. A. W. Filot, R. Pestman, R. A. van Santel, V. Petkov and E. J. M. Hensen, *Chem. Commun.*, 2014, 50, 6005–6008.

9 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.

10 D. Hibbitts, E. Dybeck, T. Lawlor, M. Neurock and E. Iglesia, *J. Catal.*, 2016, 337, 91–101. 11 G. Lauth, T. Solomun, W. Hirschwald and K. Christmann, *Surf. Sci.*, 1989, 210, 201–224. 12 J. Wang, Y. Wang and K. Jakobi, *Surf. Sci.*, 2001, 488, 83–89.

13 S. Murphy, C. Strebler, S. B. Vendelbo, C. Conradsen, Y. Tison, K. Nielsen, L. Bech, R. M. Nielsen, M. Johansson, I. Chorkendorff and J. H. Nielsen, *Phys. Chem. Chem. Phys.*, 2011, 13, 10333–10341.

Pieter van Helden replied: Without further dwelling on the differences between Co and Ru, we agree that there are some structural changes that can be expected under exposure to CO gas. The extent of these still needs to be assessed for Co. In our specific model the different sites have different saturation coverages. For the Co(111) type sites the experimental saturation coverage of 0.67 ML was implemented, while on the defect sites the only constraint was applied (allowing for up to 1 ML coverage). There is a strong possibility that CO* might saturate at higher values on the defect sites. Thus, the overall particle coverage maximum that can be attained in our model is around 0.75 ML in total. In the simulations, these are never attained due to the build up of C₂* and O* and OH* species, which compete with CO* for both terrace and defect sites. In this way it also limits the amount of CO* under steady state FT conditions.

The example of a 201 atom Ru particle in the question relates to the expansion of extremely small particles. For particles of this size, 30% or more of the atoms are located at the surface. This results in a very high total energy of the particle (due to the high surface energy) which can be significantly reduced due to binding with CO (or other adsorbates). With such high surface energies, these particles will expand and restructure in the presence of CO to lower the total energy. At larger particle sizes (as the 8 nm particle we considered in our work), less than 15% of the atoms will be located at the surface, giving a much lower total energy of the particle. These particles will not have such a large driving force to lower their surface energies as those in the range lower than 3 nm, thereby not needing excessive amounts of adsorbed CO. We are of the opinion that sites on such particles will start to approach the regime where the single crystal saturation coverages become relevant on the terrace sites. However, we concede that this still needs to be confirmed. Another indication of Co CO coverage under steady state FT is given by SSITKA work such as that shown in ref. 1. Here the steady state total coverage of CO is between 0.4 and 0.5 ML for Co size larger than 6 nm. All of the scenarios in our model give results of total Co coverage between 0.4 and 0.6 ML. In ref. 1 they show that there is an increase in the total CO coverage as the Co size decreases below 6 nm (accompanied by a decrease in activity). This could point to very small Co particles accommodating higher CO coverages, in line with the examples in the question. Alternative experimental results summarized in ref. 2 showed that dicarbonyls are formed on Co defect sites in the presence of CO pressure at low temperatures. However, it was also noted that with the addition of H₂ and increased temperature, this feature decreased significantly.

- 1 J. P. Den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen and K. P. de Jong, *J. Am. Chem. Soc.*, 2009, 131, 7197–7203.
- 2 H. Oosterbeek, *Phys. Chem. Chem. Phys.*, 2007, 9, 3570–3576.

Emiel Hensen replied: Our point of view regarding the high surface coverage is expressed in the answer to an earlier question from Kees-Jan Weststrate. In brief, high coverages are highly unlikely based on both theoretical and experimental observations. There is also no solid experimental evidence for high (> 1 ML, or even > 0.7 ML) CO coverage on Co and Ru nanoparticles. The IR bands in the work of Loveless at higher wavenumbers derive from CO adsorbed to positively charged Co (see ref. 1 and references therein). The samples in Loveless et al.² were passivated and then reduced, which appears reasonable, but then cooled in He

ow, meaning some Ru will be oxidized by trace O₂ in this way. We also refer to the IR data presented by Prof. Iglesia which clearly show that there are no di- and tricarbonyls at all and also that the CO coverage saturates at low CO pressure (much less than 1 bar), consistent with the view of Weststrate.

1 X.-Y. Quek, Y. Guan, R. A. van Santen and E. J. M. Hensen, *ChemCatChem*, 2011, 3, 1735–1738.

2 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.

Enrique Iglesia asked: You have proposed that surfaces are not at full mono-layer at typical Fischer–Tropsch synthesis conditions. In my Introductory Lecture (DOI: 10.1039/C7FD00018A), I presented infrared spectra that show saturation coverage temperatures even higher than for Fischer–Tropsch synthesis and pressures significantly lower (5–100 kPa). Volumetric uptakes of CO are consistent with CO/M surface stoichiometries of unity for >5 nm diameter Ru and Co particles and even greater than unity for smaller particles (as evident from gem-dicarbonyl bands in the infrared spectra). Saturation coverages are indeed about 0.6 ML on at extended surfaces because of their inability to relax laterally, but what is the evidence that small or large clusters of metals, and of Co and Ru in particular, cannot chemisorb stoichiometric amounts of CO?

Kees-Jan Weststrate responded: As mentioned in the reply to a related question from Prof. Neurock, there are significant differences between Ru and Co regarding which comes to the interaction with CO. As there is more data available for cobalt-based catalysts in FTS, we limit the discussion here to experimental findings on cobalt. In ref. 1 we have previously shown that on the close-packed terrace of Co the CO coverage can be pushed to 0.89 ML using a combination of low temperature and relatively high pressure. However, when we extrapolate our data to FTS temperatures and pressures, a coverage of around 0.5 is realistic. Step edge sites can indeed accommodate higher CO coverages. This is illustrated by the work of Faló, Cano and Salmeron reported in ref. 2. For small [fcc-(100)] cobalt islands on top of a Cu(100) surface, CO quantities up to 3 per cobalt surface atom were reported, but this value converged to 0.65 ML with increasing Co coverage. Likewise, on the Co(10–10) surface which exposes rows of atoms similar to step edge sites, Toomes and King report CO coverages slightly higher than 1 ML,³ confirming the notion that a local high coverage can exist at step edges. Due to this, even without invoking lattice relaxation, global CO coverages higher than 0.5 can be accommodated on cobalt nanoparticles. SSITKA measurements provide in situ information about the CO coverage under working conditions. Den Breejen et al. report a CO coverage of 0.43 ML on ~8 nm Co particles under methanation conditions, with p_{CO} ¼ 55 mbar at 210 C.⁴ In ref. 5, Mims et al. report similar data, but measured at 0.4 bar CO, and 202 C. Their Co/SiO₂ catalyst has a cobalt metal loading of 23% with a dispersion of 2.8% (~35 nm). This translates to a cobalt surface atom concentration of 109 000 nmol g⁻¹ catalyst. The reported concentration of reversibly bound CO is 60000 nmol per g catalyst, yielding a 0.55 ML CO coverage in this case. Thus, in situ quantification of the CO coverage provides evidence for a CO coverage lower than 1 ML under FTS conditions. On at Co single crystal surfaces a CO concentration of 1 ML is highly unfavourable due to adsorbate interactions. Yet several authors report FTS activity on such surfaces,^{6,7}

and indicate that long chains can grow.⁸ This illustrates that a CO concentration close to unity is not essential for the growth of long chains.

- 1 C. J. Weststrate, J. van de Loosdrecht and J. W. Niemantsverdriet, *J. Catal.*, 2016, 342, 1–16.
- 2 F. Faló, I. Cano and M. Salmerón, *Surf. Sci.*, 1984, 143, 303–313.
- 3 R.L. Toomes and D.A. King, *Surf. Sci.*, 1996, 349, 1–18.
- 4 J. P. Den Breejen, P. B. Radstake, G. L. Bezemer, J. H. Bitter, V. Frøseth, A. Holmen and K. P. de Jong, *J. Am. Chem. Soc.*, 2009, 131, 7197–7203.
- 5 C.A. Mims, L.E. McCandlish, *J. Phys. Chem.*, 1987, 91, 929–937
- 6 J.J.C. Geerlings, M.C. Zonneville and C.P.M. de Groot, *Surf. Sci.*, 1991, 241, 315–324.
- 7 M. Ehrensperger and J. Wintterlin, *J. Catal.*, 2014, 319, 274–282.
- 8 V. Navarro, M.A. van Spronsen, J.W.M. Frenken, *Nat. Chem.*, 2016, 8, 929–934.

Michael Bowker remarked: We appear to have a disagreement between the single crystal work and the catalysts work with regard to coverages by CO, however, it seems to me that there is not so much of a problem. ‘Curved’ surfaces, such as on small nanoparticles, enable better separation of the O ends of adjacent CO molecules, which then reduces O–O repulsion and results in a higher strength of adsorption, all other effects ignored, at the same coverage in the high coverage regime. Furthermore, it means that the same repulsion energy (which reduces adsorption energy) only occurs at a higher coverage on curved nanoparticles. In a similar vein, steps act like curved surfaces, at least in the sense that they provide the facility for the staggering of CO-surface bond angles to minimise repulsion.

Matthew Neurock replied: The different coverages reported on particles and single crystal surfaces are the result of: 1) the different pressures used under UHV studies on single crystal surfaces and catalytic studies on supported particles, and 2) the differences in the surface structures of the single crystals and metal particles. Most of the surface science studies carried at UHV conditions (10^{-7} – 10^{-8} torr) report coverages on Co(0001) and Ru(0001) surfaces of ~0.67 ML CO. A recent UHV study of CO adsorption on Ru(0001) showed that increasing the CO pressure from 10^{-8} torr to 0.1 torr increased the CO coverage from 0.67 ML to ~0.9 ML of CO.¹ It is important to note that Fischer–Tropsch is carried out at significantly higher pressures (> 1 atm). In addition to the changes in pressure, the repulsive interactions between neighboring COs on the particles is different than that on the surface. Surface curvature and edge sites present on the particles allow the CO to ‘fan’ outwards away from the particle and neighboring COs to reduce repulsive O–O interactions as you point out. A second factor that leads to higher coverages on the particles over those found on single crystal surfaces is the ability of the particle to expand radially to reduce the repulsion between the coadsorbed CO. The outer metal atoms relax outward and result in more ‘curved’ surfaces, even for the larger metal particles. This enables the COs to ‘fan’ away from one another and significantly reduce the repulsive O–O interactions. This is clearly seen in EXAFS experiments carried out at higher pressures of CO on different metals reported in the literature. Single crystal surfaces can only expand perpendicular to the surface at high CO coverages, which does not allow for a significant reduction in repulsion from O–O interactions. As such, single crystal surfaces reconstruct to relieve the strain that results from repulsive interactions that occur at higher coverage or limit surface coverages to 0.6–0.7 ML CO. The coverage and interactions of CO on edges and corner sites may be rather different as the coordinatively unsaturated metal sites can take up more than 1 CO to form

di- and tri-carbonyls analogous to what is seen on single metal atom organometallic systems. Infrared spectral data taken at high CO pressures on supported Ru particles show clear evidence of di-carbonyl bands. This is supported by theoretical calculations, which report the presence of di-carbonyls and tri-carbonyls at edge and corner sites on Ru₂₀₁ clusters.²

1 D.E. Starr and H. Blum, *Surf. Science*, 2013, 608, 241–248.

2 B. T. Loveless, C. Buda, M. Neurock and E. Iglesia, *J. Am. Chem. Soc.*, 2013, 135, 6107–6121.

Avelino Corma enquired: How many active sites do you need to continue the reaction and how many types of sites? From a kinetic point of view there are fewer species on the surfaces – they need to find themselves to react. Frequency factor of the reaction goes down a lot.

Emiel Hensen answered: Remembering our live discussion, the issue raised by Prof. Corma is interesting. Does a chain grow using CH_x species from one CO dissociation site or are more sites involved? This is of course very difficult to probe experimentally. It would require titrating the step-edge sites and then establishing the relation between chain-growth probability and step-edge density. In our previous work on aqueous phase FTS we have found indications that more step-edge sites does not lead to a different chain-growth probability so that it seems that one CO dissociation site is linked to one chain growth site. Of course, we should admit that we understand even less about aqueous phase FTS compared with conventional FTS.¹

Microkinetics simulations cannot answer such question as we assume mean field. We expect that diffusion on the crowded surface will be rather slow so that it is reasonable to assume that CO dissociation and chain growth are closely linked at the surface. CO dissociation needs to be sufficiently fast, and chain growth needs to be fast in comparison with chain growth termination. Computationally, kinetic Monte Carlo could help to simulate the role of diffusion, which is of course exceedingly challenging for this particular reaction.

1 X.-Y. Quek, R. Pestman, R. A. van Santen and E. J. M. Hensen, *Catal. Sci. Technol.*, 2014, 4, 3510–3523.

Pieter van Helden also replied: In our microkinetic work we did not assume a single site a priori, but tried to simulate the actual FCC Co particle. What we do see in our model is that most of the surface sites have a high coverage of CO, thus the effective number of active sites are much lower than the total number of a specific site. Allowing for interaction between sites, we see, arising from the simulation results, that at least two types of sites seem to be necessary for FT on FCC Co: one to facilitate the CO scission process and one where chain growth occurs. On closer inspection of our results, we also see another site being active for chain growth, but at an order of magnitude slower than the overall reaction rate. This site also becomes a store of spectator species. This gives an indication of the mechanistic complexity that underlies the FT reaction on actual nanoparticles.

Hans Schulz commented: Molecular modeling in Fischer–Tropsch synthesis is challenging because of extreme complexity. Advanced models are being

developed, however further pertinent questions prevail. With cobalt as catalyst the steady state of reaction is only attained during a certain time, with changing rate and selectivity, indicating self-organization of the FT-regime (see Fig. 2, le - side).

(1) Increasing CO-conversion from 10 to 30%; (2) Chain growth probability (range $C_3 - C_7$), increasing from 60 to 90%, (3) Olefin content (in C_3), increasing from 30 to 50%, (4) Olefin-1 among n-olefins in C_4 , increasing from 20 to 50%, (5) Chain branching probability (pbr4), decreasing from 10 to 4%.

As shown in Fig. 2, right-side, the typical pattern of chain branching probability over the carbon number (chain length) at steady state (8620 min on stream) exhibits an exponential decline with an increasing carbon number, as is thought to reflect increasing spatial constraints with increasing size of chains. The first value (at C_3) is exceptionally low, as assumed to be caused by a particular steric constraint to desorption, applying to the involved tertiary C-atom (for desorption of isobutene, respectively isobutane). Initially, e.g. at 100 min reaction time, branching probability is much higher than at steady state, indicating less spatial constraints on growth sites. Also, a different pattern is observed, indicating a further branching reaction, which increases with carbon number (from C_5 to higher C-numbers). This opposite C-number-dependence is thought to result from the carbon number increasing and olefin re-adsorption on growth sites being now possible with the carbon atom 2 because of lower spatial constraints prevailing.

As a further controlling principle, specific barriers against migration of intermediates between catalyst sites can be imagined.

1 H. Schulz, Catal. Today, 2014, 228, 113–122.

Kees-Jan Weststrate replied: Model experiments and theory calculations on well-defined surfaces focus on the elementary surface reaction steps and micro-kinetics are used to explore the interplay between various elementary reaction steps to highlight and provide insights into the factors that determine the activity and selectivity. With respect to olefin selectivity, some studies exist where the effect of chain length was studied by theoretical means, see e.g. ref 1. Also, in our recent publication we report distinct reactivity differences between ethene and propene on a Co surface, which can contribute to the typical deviation of C_2 products from the typical selectivity pattern. I am unaware of theoretical studies

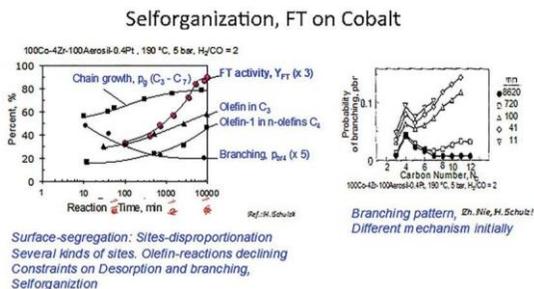


Fig. 2 Selforganization FT on cobalt.

that explore the mechanism of the formation of branched products on cobalt catalysts. In the initial phases, the catalyst is modified in several ways. One notable effect is the build-up of wax inside the pores, and on the surface of the catalyst particles as well³, on a time scale of hours. Further relatively slow changes that occur on the time scale of days include carbon deposition and sintering, which would both affect the catalytic surface. The impact of these factors is typically not taken into account in the model studies at present. The high coverage of the surface under reaction conditions was identified as an important factor during the discussion. The influence of how lateral interactions, both steric and electronic, affect the stability of surface intermediates which translates to selectivity differences appears to be an important direction for future research.

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