

Catalysis in MOFs: general discussion

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Jet-Sing Lee opened a general discussion of the paper by Frederik Haase: Can you comment on how the band positions of PTP-COF compares with the Nx-COFs that you calculated by modelling? Have you tried measuring these experimentally by cyclic voltammetry (CV)? And if so, how well do they compare with your models?

Frederik Haase replied: Calculated orbital energy positions for selected precursor aldehydes are shown in the Supporting Information (Fig. S13 and S14) (DOI: c7fd00051k), including the ones of the Nx-COF series. This comparison shows that PTP-CHO has similar HOMO and LUMO levels as N1-CHO, in line with the observed photocatalytic activity.

We have tried to determine the band positions experimentally for the Nx-COFs by CV but were unable to see reproducible oxidation and reduction peaks indicative of the band positions of the LUMO, which we primarily attribute to the low conductivity of these covalent organic frameworks (COFs) and the difficulty in obtaining thin, adhesive films of these materials. Further, we have attempted to determine the band positions by means of Mott-Schottky measurements; however, since it is not known if a space charge region is present (a prerequisite for attributing the capacitance in a MS plot to a flat band potential), it is difficult to extract meaningful band positions from the data.

Pascal Van Der Voort said: I enjoyed your talk about covalent organic frameworks. You show in the paper that the surface area is on the low side as well as the crystallinity, and you give several explanations for that. There might be another explanation. Have you looked at this using TEM? We recently saw that some COFs have crystalline patches amongst huge areas of amorphous material.¹ This

may explain the observations on the surface area and crystallinity. Have you tried this and do you think this might be a possibility?

1 P. Van Der Voort, L. Banning, *et al.*, unpublished results.

Frederik Haase answered: We have observed the crystallinity in COFs to be electron beam sensitive. This beam sensitivity becomes all the more important with COFs of low crystallinity and we do not observe lattice fringes anywhere throughout the whole sample for other COFs that are not so crystalline. We thus did not investigate PTP-COF with TEM. The fact that we observe broad reflections in the X-ray powder diffraction pattern is indicative of small crystallites full of disorder, rather than a “crystalline-among-amorphous” scenario. However, a low percentage of crystalline particles would lead to sharp reflections that could be superimposed with the broad reflections, but are invisible due to their low intensity. It may thus very well be that only parts of the sample are crystalline and it would be possible to investigate the amorphous fraction of the sample with the help of quantitative phase analysis, but we have not performed these experiments so far.

Pascal Van Der Voort queried: If you model the perfect material, using density and pore size, what surface area and pore volumes would you expect compared with what you have now?

Frederik Haase responded: The theoretical surface area of the PTP-COF is $2147 \text{ m}^2 \text{ g}^{-1}$ but the measured BET area is $84 \text{ m}^2 \text{ g}^{-1}$. The theoretical pore volume is $0.95 \text{ cm}^3 \text{ g}^{-1}$ vs. $0.23 \text{ cm}^3 \text{ g}^{-1}$ in the measured sample. Hence, the discrepancy is obvious, pointing to real structure effects (stacking faults and other defects) or morphology effects that decreases the surface area substantially.

Wenbin Lin asked: You show the activity in microliters per gram catalyst per hour, which is equivalent to 0.5 turnover per unit per hour. Is this calculation correct? Have you thought about using a porphyrin? Or incorporating cobalt in the core of the COF?

Frederik Haase responded: We reported the activity as $83.83 \mu\text{mol h}^{-1} \text{ g}^{-1}$, since in the heterogeneous system we study the number of active sites is not known. The turnover can be estimated based on the platinum co-catalyst nanoparticles, on the surface of which hydrogen is produced electrocatalytically. If we assume that every platinum atom added to the reaction mixture for photo-deposition in fact adheres to the COF surface and that every single atom of the nanoparticle is an active site, the turnover rate would be approx. 0.34 per hour. This however dramatically underestimates the actual turnover rate, since not all platinum that is added to the reaction mixture is deposited onto the COF and since only the surface atoms of the platinum nanoparticles are active in generating hydrogen.

The use of molecularly defined metal-containing co-catalysts such as cobalt complexes would enable a more accurate determination of the turnover rate and also allow for a higher level of control of the interface of the co-catalyst with the photocatalyst. This is an avenue we are currently pursuing, for example in the

poster presented by a colleague, Dr Tanmay Banerjee, at this Faraday Discussions meeting.

Aron Walsh asked: The one hour activation period for hydrogen evolution is curious. In the paper you ascribe this to the formation of Pt nanoclusters. Firstly, is there any direct evidence for this? Secondly, if you cycle a second time is a similar activation step required?

Frederik Haase responded: Unfortunately, we have no direct evidence for the causal relationship between the activation period and the platinum depositions. However, the photodeposition of platinum nanoparticles is a well known and frequently used method for the *in situ* synthesis of the hydrogen evolution co-catalyst.¹ The deposition of platinum takes time to complete,² therefore sub-optimal platinum loadings at the beginning of the photocatalysis experiment would lead to slower than steady state hydrogen evolution rates during the activation period. Although we have not tested the cycling of the photocatalyst, we would speculate that an activation period solely based on the generation of platinum nanoparticles would vanish once it is cycled.

1 Z. Jiang, Z. Zhang, W. Shangguan, M. A. Isaacs, L. J. Durdell, C. M. A. Parlett and A. F. Lee, *Catal. Sci. Technol.*, 2016, **6**, 81–88.

2 J. Ma, A. Habrioux and N. Alonso-Vante, *J. Solid State Electrochem.*, 2013, **17**, 1913–1921.

Duncan Woods said: The correlation between your calculated radical anion stabilisation energies and the photocatalytic activities of these materials is striking. What weight do you give these calculated energies as a factor in determining these photocatalytic activities relative to the other factors discussed here? Have you tried applying these calculations to other classes of materials and, if so, is the relationship also observed?

Frederik Haase replied: Weighting of the various individual contributions to the photocatalytic activity is difficult, as they cannot systematically be disentangled or varied independent of each other in this system. While there are of course many possible influences such as, *e.g.*, crystallinity, surface area, or conductivity, the observed correlation is a strong hint that the radical anion stabilization may be a major factor in determining the photocatalytic hydrogen evolution activity of our materials. In addition, we have further independent experimental evidence from transient absorption studies of modified Nx-monomers, to be published elsewhere, that radical anions are indeed encountered under photocatalytic conditions in this material system. We have not applied the concept of radical anion stabilization to other materials than COFs yet.

Mircea Dincă stated: You wrote a very elaborate discussion on the effect of conformational changes on activity. How reasonable is it to have this discussion when not knowing about the crystallinity of the material?

Frederik Haase replied: Our main goal in discussing the possible conformers was to explain the observed crystallinity rather than directly rationalize the activity. Of course the crystallinity will play a role in determining the activity of the

material, but whether there is a direct correlation between conformers and activity is unknown. We expect that the conformational analysis of building blocks could be used in estimating the expected crystallinity of a COF, much like you previously rationalized the different observed crystallinities resulting from angled vs. straight COF linkers.¹

1 G. H. V. Bertrand, V. K. Michaelis, T.-C. Ong, R. G. Griffin and M. Dincă, *Proc. Natl. Acad. Sci. U. S. A.*, 2013, **110**, 4923–4928.

Wenbin Lin opened a general discussion of the paper by Carlo Lamberti: You also mentioned the possibility of activating methane – it would be interesting if you could do that. The only example I know in catalytic methane activation is to use fuming sulfuric acid to get methyl sulfate. Will the MOF be stable?

Carlo Lamberti replied: Our functionalized UiO-67 MOFs will certainly not survive exposure to fuming sulfuric acid, as used in homogeneous catalysis. However, while the aggregated Pt species formed in the UiO-67-Pt sample after activation under concentrated H₂ flow (10% H₂ in He) exhibit activity in CO₂ conversion,¹ the UiO-67-Cu sample activated in inert conditions may be of potential interest for methane activation. This potential interest is related to the fact that UiO-67-Cu exhibits isolated (not aggregated) Cu centers like those present in zeolitic frameworks that have been shown to be interesting systems for methane activation.^{2–5} We plan to investigate along this direction in the near future but we have no results so far.

1 E. S. Gutterød, S. Øien-Ødegaard, K. Bossers, A.-E. Nieuwelink, M. Manzoli, A. Lazzarini, L. Braglia, E. Borfecchia, S. Ahmadigoltapeh, B. Bouchevreau, B. T. Lønstad-Bleken, R. Henry, C. Lamberti, S. Bordiga, B. M. Weckhuysen, K. P. Lillerud and U. Olsbye, *Ind. Eng. Chem. Res.*, 2017, **56**, DOI: 10.1021/acs.iecr.7b01457.

2 M. H. Groothaert, P. J. Smeets, B. F. Sels, P. A. Jacobs and R. A. Schoonheydt, *J. Am. Chem. Soc.*, 2005, **127**, 1394–1395.

3 V. L. Sushkevich, D. Palagin, M. Ranocchiari and J. A. van Bokhoven, *Science*, 2017, **356**, 523–527.

4 M. Ravi, M. Ranocchiari and J. A. van Bokhoven, *Angew. Chem., Int. Ed.*, 2017, DOI: 10.1002/anie.201702550.

5 D. Pappas, E. Borfecchia, M. Dyballa, I. Pankin, K. L. Lomachenko, A. Martini, S. Teketel, B. Arstad, G. Berlier, C. Lamberti, S. Bordiga, U. Olsbye, K. P. Lillerud, S. Svella and P. Beato, *J. Am. Chem. Soc.*, 2017, submitted.

Dirk Volkmer stated: In your manuscript (DOI: c7fd00024c) you show in Fig. 3(c) the reduction of a [Pt(II)Cl₂(bipy)] coordination unit with molecular H₂ (gas), yielding a coordinatively highly unsaturated [Pt(0)(bipy)] species. Did you try to characterize this open metal site by gas sorption, *i.e.* binding small molecules (*e.g.* CO) to the Pt(0) center?

Carlo Lamberti replied: The UiO-67-Pt sample activated under continuous gas flow of diluted H₂ (3% H₂ in He, activation followed by X-ray absorption spectroscopy (XAS) in Fig. 2) has been successively characterized by room temperature FTIR spectroscopy of adsorbed CO.¹ The spectrum reported a doublet at 2126 and 2090 cm⁻¹, ascribed to dicarbonyl adducts on isolated framework Pt sites. Upon successive thermal activation at increasing temperatures (up to 473 K), the doublet progressively decreases in intensity resulting in a single broad component centred at 2105 cm⁻¹, and ascribed to the corresponding monocarbonyl

adduct. No bands due to CO adsorbed on Pt nanoparticles have been observed in that experiment. Very recently the same FTIR experiment has been repeated on a UiO-67-Pt sample activated under concentrated H₂ flow (10% H₂ in He, activation followed by XAS in Fig. 6) and the typical bands due to CO adducts on Pt metal nanoparticles have been observed.²

- 1 S. Øien, G. Agostini, S. Svelle, E. Borfecchia, K. A. Lomachenko, L. Mino, E. Gallo, S. Bordiga, U. Olsbye, K. P. Lillerud and C. Lamberti, *Chem. Mater.*, 2015, **27**, 1042–1056.
- 2 L. Braglia, E. Groppo *et al.*, manuscript in preparation.

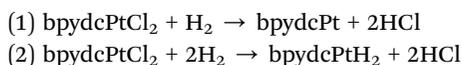
Dirk Volkmer commented: In your manuscript (Fig. 8(d)) you show a [Cu(II)Cl–(OH–)(bipy)] coordination unit, which gets reduced to a [Cu(I)Cl–(bipy)] upon “mild thermal treatment in an inert atmosphere”, as stated in the text. What stoichiometric reaction do you suggest for this particular transformation, given the fact that it occurs at a single metal site and in the absence of any solvent?

Carlo Lamberti responded: We do not have a locally balanced stoichiometric reaction to infer for the structural and electronic changes undergone from the divalent bpydcCuClOH to the monovalent bpydcCuCl site by thermal activation in inert gas. In the adopted experimental conditions the fraction of solvent present in the sample is indeed negligible (below the detection from IR spectroscopy), but there is still a fraction of water as the post synthesis functionalization implies that the UiO-67-bpy MOFs interact with CuCl₂ in aqueous solution. The water excess is removed along the activation process followed by XAS in Fig. 8 that result in the virtually total Cu(II) to Cu(I) reduction. This phenomenon is very similar to what has been observed in the last two decades in the Cu-zeolite literature and referred to as the “self-reduction” process of Cu(II),^{1–5} the locally balanced stoichiometric reaction of which is still under debate.

- 1 S. C. Larsen, A. Aylor, A. T. Bell and J. A. Reimer, *J. Phys. Chem.*, 1994, **98**, 11533–11540.
- 2 G. T. Palomino, P. Fiscaro, S. Bordiga, A. Zecchina, E. Giamello and C. Lamberti, *J. Phys. Chem. B*, 2000, **104**, 4064–4073.
- 3 F. X. Llabres i Xamena, P. Fiscaro, G. Berlier, A. Zecchina, G. T. Palomino, C. Prestipino, S. Bordiga, E. Giamello and C. Lamberti, *J. Phys. Chem. B*, 2003, **107**, 7036–7044.
- 4 E. Borfecchia, K. A. Lomachenko, F. Giordanino, H. Falsig, P. Beato, A. V. Soldatov, S. Bordiga and C. Lamberti, *Chem. Sci.*, 2015, **6**, 548–563.
- 5 A. Martini, E. Borfecchia, K. A. Lomachenko, I. Pankin, C. Negri, G. Berlier, P. Beato, H. Falsig, S. Bordiga and C. Lamberti, *Chem. Sci.*, 2017, **8**, DOI: 10.1039/c7sc02266b.

Connie Lu said: Continuing that question, I also suspect that the Pt species is a dihydride complex. Have you tried to use deuterium (D₂) and look for the Pt–D stretching frequency?

Carlo Lamberti replied: In the already mentioned work,¹ for the UiO-67-Pt sample activation under a continuous gas flow of diluted H₂ (3% H₂ in He, activation followed by XAS in Fig. 2) we hypothesized the following two reactions:



Reaction (1) was preferred, because we do not have clear evidence for the Pd–H stretching frequency nor other spectroscopic fingerprints ascribable to the

probable bpydcPtH intermediate species in reaction (2). Nevertheless, the two final species, bpydcPt and bpydcPtH₂, are virtually indistinguishable from EXAFS. In this respect, we agree with your suggestion that experiments with either D₂ or ¹³CO would be very informative, enhancing the sensitivity in the detection of possible bpydcPtH₂ complexes by FTIR. We hope to be able to follow your suggestion in the near future.

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

Mircea Dincă asked: What percentage of Pt stays as single atom Pt(0), and what percentage goes to Pt nanoparticles?

Carlo Lamberti replied: In the experiments performed so far, changing the H₂/inert ratio and changing the overall flux, we were able to tune the percentage of Pt in the nanoparticle phase from 0% up to 40%, keeping intact the UiO-67 framework. Possibly, a higher fraction of Pt nanoparticles may be reached by further increasing the H₂/inert ratio.

Monique van der Veen opened a general discussion of the paper by Connie C. Lu: For the cobalt structures you make, you start from a well-defined ligand, and you show the potential cobalt structure based on DFT calculations and this ligand. Do you have any experimental evidence that you indeed make the structures you propose?

Connie Lu responded: The experimental data presented in this paper strongly demonstrates that: (1) the stoichiometry of the bimetallic complexes inside the MOF is one per hexazirconium node, and (2) the bimetallic complexes are attached to the Zr₆ nodes in the small pore. We did not, however, obtain data that provides a detailed structure of the active site, *e.g.* EXAFS or single crystal X-ray diffraction. The structures shown in the paper are based on DFT calculations. In unpublished work, we have obtained EXAFS data of analogous bimetallic species that does show a short intermetal distance, in support of an intact bimetallic unit, and furthermore, coordination of the N-donors of the ligand.

Mohamed Eddaoudi asked: How can you go from a MOF to a silica-based framework? How sure are you that you have the targeted topology or morphology? In other words is the resultant framework 3-periodic and mainly silica-based?

Connie Lu responded: In transforming the MOF materials to a silica-based framework, the paper shows the high-angle annular dark field (HAADF) images prior to and post-nanocasting (Fig. 4 and 5). Comparison of these images shows that the morphology of the original MOF particle is retained in the silica materials. The topology of channels in the silica materials has been shown in a previous study, where only the MOF was nanocast.¹ A similar question has been posed by Pascal Van der Voort concerning the periodicity of the silica-framework materials, and I can refer you to our response to this question. The SiO₂ nanocast

materials are indeed mainly silica based, with approximately 50 to 60 Si atoms per Zr₆ node (Table 1).

1 C. D. Malonzo, S. M. Shaker, L. Ren, S. D. Prinslow, A. E. Platero-Prats, L. C. Gallington, J. Borycz, A. B. Thompson, T. C. Wang, O. K. Farha, J. T. Hupp, C. C. Lu, K. W. Chapman, J. C. Myers, R. L. Penn, L. Gagliardi, M. Tsapatsis and A. Stein, *J. Am. Chem. Soc.*, 2016, **138**, 2739–2748.

Mohamed Eddaoudi commented: Do you have layers sitting on the surface? Does this result in an inverted type of net? All you have left is mostly inorganic parts. Do the nodes (original polynuclear clusters) stay because they interact directly with the silica?

Connie Lu responded: After infiltration of the MOF with the silica precursor (TMOS), the material is washed with methanol to remove excess TMOS on the external surface. The HAADF image of the post-nanocast material does not show an excess of silica layers on the surface (Fig. 5). The resulting nanocast will be somewhat inverted relative to the MOF template. The silica nanocast of NU-1000, *i.e.* the unfunctionalized MOF, retained channels, as observed by TEM, so we propose the silica framework as portrayed in Fig. 1.¹ With reactive OH groups on the nodes, TMOS should be able to condense on the nodes as well, and perhaps due to this covalent attachment, the original nodes remain site-isolated in the silica nanocasts.

1 C. D. Malonzo, S. M. Shaker, L. Ren, S. D. Prinslow, A. E. Platero-Prats, L. C. Gallington, J. Borycz, A. B. Thompson, T. C. Wang, O. K. Farha, J. T. Hupp, C. C. Lu, K. W. Chapman, J. C. Myers, R. L. Penn, L. Gagliardi, M. Tsapatsis and A. Stein, *J. Am. Chem. Soc.*, 2016, **138**, 2739–2748.

Wenbin Lin stated: I can think of a control experiment – take a Pt compound, put it on mesoporous silica and calcine it. Do you see the same sort of reactivity? This may show if the method is advantageous or if you need other support methods.

Connie Lu replied: Thank you for the suggestion. It would be a useful control reaction for the late metals. On a related sample, we did compare the nanocast of NU-1000 to a calcined sample made from mixing hexazirconium clusters with mesoporous silica. While the NU-1000 precursor showed no evidence of Zr agglomeration after calcination, the control sample from mesoporous silica did.

Marco Ranocchiari remarked: You start with a well-defined cobalt complex stabilized by ligands. You then cast and burn off organics. The cluster seems to be intact but how is it stabilized? It is missing the ligands now.

Connie Lu replied: The original ligand donors will be replaced by the O-donors from the node and/or O₂ during calcination. The removal of the ligand is expected to form bimetallic oxide clusters that are more closer to bioinorganic active sites. We also anticipate that the metal–metal interaction in the well-defined bimetallic precursor will be destroyed, *e.g.* by bridging O/OH ligands, in the calcined and nanocast materials.

Pascal Van Der Voort asked: Normally nanocasting is done in dense porous systems, such as carbon or silica. Here you use a MOF as the template for the casting, but it has hollow and thin pore walls. You show it in Fig. 1 as a thick silica film deposited on MOF walls. What kind of evidence do you have that this is actually happening and that the TMOS does not penetrate the entire MOF structure?

Connie Lu answered: (Andreas Stein, the co-corresponding author of the paper, responded to this query.) Multiple pieces of evidence for the schematic model for $\text{SiO}_2@NU-1000$ with a surface coating on the walls of the 3 nm mesopores in NU-1000 were presented in the previous publication on nanocasting NU-1000.¹ Evidence is most clearly seen in the difference envelope density analysis (see Fig. 3b in ref. 1) that shows additional electron density after infiltration of the infiltrated material mainly in the 3 nm pores with almost no electron density in the 1 nm triangular channels. Most electron density is on the wall surface with some density near the center, which could indicate partial filling of the mesopores in parts of the structure. The channels are not likely to be completely filled with silica even if all the pore space is filled with the precursor (TMOS), because of volume shrinkage after the loss of MeOH and silica condensation. Additional evidence comes from N_2 sorption experiments (see Fig. 3a in the manuscript) that show a reduction in pore volume and shift to smaller pore diameters after silica infiltration. The extent of infiltration and location of the scaffold depends on the precursor, and we have observed different filling for some other (non-silica) precursors (manuscript in preparation). After removal of the organic linkers ($\text{Zr}_6@SiO_2$), porosity and access to the clusters is maintained, as illustrated by N_2 sorption experiments (Fig. S10 in ref. 1), however, the pore structure is less periodic than in NU-1000 or in $\text{SiO}_2@NU-1000$ (Fig. 5f in ref. 1), pore volume is reduced, and the pore size distribution is broader. Nonetheless, the crystal morphology is maintained (with some shrinkage) and mesopores are still oriented along the original direction. The schematic for $\text{SiO}_2@NU-1000$ is necessarily over-simplified, but it still illustrates the situation to a good approximation. Some bond formation between the oxozirconium clusters and silica cannot be excluded; it is likely, on the basis of the DFT calculations.

1 C. D. Malonzo, S. M. Shaker, L. Ren, S. D. Prinslow, A. E. Platero-Prats, L. C. Gallington, J. Borycz, A. B. Thompson, T. C. Wang, O. K. Farha, J. T. Hupp, C. C. Lu, K. W. Chapman, J. C. Myers, R. L. Penn, L. Gagliardi, M. Tsapatsis and A. Stein, *J. Am. Chem. Soc.*, 2016, **138**, 2739–2748.

Pascal Van Der Voort said: To follow up on my previous question: silica should be stable in electron microscopy, can you see the silica structures in this way? Can you see the pores like they are drawn in the manuscript?

Connie Lu answered: The structure of the silica scaffold was closely examined in the previous publication on nanocasting NU-1000.¹ Fig. 5 in that paper shows TEM images with highly parallel, uniform channels in NU-1000 (Fig. 5d), similar parallel and slightly less ordered uniform channels in $\text{SiO}_2@NU-1000$, and unidirectional, even less ordered channels in $\text{Zr}_6@SiO_2$.

1 C. D. Malonzo, S. M. Shaker, L. Ren, S. D. Prinslow, A. E. Platero-Prats, L. C. Gallington, J. Borycz, A. B. Thompson, T. C. Wang, O. K. Farha, J. T. Hupp, C. C. Lu, K. W. Chapman, J. C. Myers, R. L. Penn, L. Gagliardi, M. Tsapatsis and A. Stein, *J. Am. Chem. Soc.*, 2016, **138**, 2739–2748.

Mircea Dincă commented: Regarding the nanocast materials, there must be information in the literature on the mobility of cobalt oxide or cobalt ions on silica. Diatomic clusters may stay put on a silica surface. There are many examples of amorphous cobalt oxides. Can you tell if the CoO nanoparticles agglomerate on the surface?

Connie Lu replied: In most literature involving CoO modification of silica, there is little or no control over CoO cluster size, their distribution and dispersion. The method involving NU-1000 modification with bimetallic clusters facilitates greater uniformity and better dispersion than what has been achieved before. After nanocasting, we did not see any evidence of CoO agglomeration by XRD or electron diffraction (ED). In contrast, in some Ni-modified nanocast NU-1000 samples prepared by other approaches we saw evidence for agglomeration by XRD or ED (unpublished data). However, the absence of XRD/ED reflections does not preclude formation of very small or non-crystalline CoO clusters. The best (indirect) evidence for maintaining discrete bimetallic clusters after nanocasting is the similar performance of the $(\text{py}_3\text{tren})\text{Co}_2@\text{NU-1000}$ samples and the nanocast $\text{Co}_2\text{Zr}_2@\text{SiO}_2$ samples in catalytic tests.

Mircea Dincă began a general discussion: Many of us in the community make a catalyst, and wonder what catalysis it will do, *e.g.* make single site, and think what can I do with it. The other approach is to identify a problem, and then provide a solution by making a MOF/porous catalyst for said process. Which approach is better, if either, and what can we do to put MOFs on the map for heterogeneous catalysis?

Marco Ranocchiari replied: Many have asked what is the right way to use MOFs in catalysis. Any MOF that can drive selectivity in a unique way for a process can be potentially commercialized. Replacing existing large-scale processes is not attractive for the industry and simply “heterogenizing” a homogeneous system is not enough. There must be added value that justifies the need for a complex—and expensive—material. To put MOFs on the map for heterogeneous catalysis we not only need a proof-of-concept that shows that they can do unique things in catalysis but also have a concrete problem that the industry, likely the fine-chemical one, needs to solve. We wrote a perspective in 2011 discussing some aspects highlighted during this symposium.¹ Even though the examples are not the most recent, the part about designing future catalysts might be worth a read.

1 M. Ranocchiari and J. A. van Bokhoven, *Phys. Chem. Chem. Phys.*, 2011, **13**, 6388–6396.

Wenbin Lin remarked: We have a 15–20 year advantage! The strategy has evolved and now I am more convinced that MOFs have major applications in catalysis. What collectively can the community do to ensure this? It doesn't matter how you go about solving the problem if you get a good outcome. For example, for

the transformation of ethane to ethylene or propane to propylene, MOFs are ideal for medium to large scale syntheses.

Omar Farha commented: I sort of agree with Wenbin – high value, low volume products to commercialise MOFs, but we shouldn't be scared to tackle bigger markets.

Carlo Lamberti remarked: In the field of shape selective catalysis, zeolites have the advantage of higher stability, while MOFs have the advantage of higher flexibility. So far, an additional important advantage of zeolites is the much longer experience that industrial and academic laboratories had in testing, scaling-up and optimizing catalytic reactions. This experience extends over several decades, while academic attempts to perform heterogeneous catalysis in MOFs are much younger. It is therefore not surprising that no industrial process is at present active using a MOF-based catalyst. On the industrial scale, several years are needed to promote a promising catalytic reaction from the laboratory scale, through the pilot scale and finally to the industrial scale. Just as an example, the isomorphous substitution of a few wt% of Ti(IV) in the silicalite-1 framework (MFI) led to the TS-1 catalyst, relevant for the oxidation of several important organic compounds using hydrogen peroxide as the oxidizing agent.^{1,2} The catalyst was patented by ENI at the beginning of the eighties,³ but only two decades later the first industrial plants based on TS-1 were realized in Japan by Sumitomo and in Germany by BASF. I consequently believe that the age of MOFs as industrially relevant catalysts has simply not arrived yet. In this regard, I believe that probably the most promising field for MOFs is related to the catalysis for pharmaceutical products, where reactions run at low temperatures, the reactor loading capacity is within the tens or hundreds of Kg range, and where the high economical value of the produced molecules will easier compensate for the higher cost of MOFs synthesis.

1 B. Notari, *Adv. Catal.*, 1996, **41**, 253–334.

2 S. Bordiga, F. Bonino, A. Damin and C. Lamberti, *Phys. Chem. Chem. Phys.*, 2007, **9**, 4854–4878.

3 M. Taramasso, G. Perego and B. Notari, *US Pat.*, 4410501, 1983.

Frederik Haase added: I think one of the best applications of MOFs and other defined porous materials in catalysis is by using reactions that can only be performed in these materials. We have seen some examples at this Faraday Discussion of molecularly defined catalysts that would not be possible in classical heterogeneous or homogeneous systems. Examples are highly coordinatively unsaturated metal complexes that would normally deactivate through dimerization. I think that these metal complexes and other reactive groups with low steric hindrance such as carbenes or frustrated Lewis acid base pairs present significant opportunities for new chemistry, which can only be performed with porous materials.

Mohamed Eddaoudi opened a general discussion of the paper by Wenbin Lin: You have shown how employing MOFs as scaffolds to immobilize a periodic array of catalytic centers (heterogeneous catalyst) is helping to improve the associated conventional homogeneous catalysis. What makes you now (after 20 years) believe that these MOFs are now able to perform better than earlier MOFs and that are good prospects for catalysts for the future?

Wenbin Lin responded: More stable MOF scaffolds like the UiO family are available now and more researchers with proper training and backgrounds are entering MOF catalysis research. I believe that MOF catalysis is not simply about immobilizing known catalysts onto a support any more. MOFs offer a new way of thinking about and designing molecular catalysts that cannot be made in any other way.

Mohamed Eddaoudi asked: Do you believe that the recent promising progress in MOFs for catalysis is mainly due to the emergence of relatively more stable MOFs such as Zr-based UiO-66 analogues? Are MOFs based on Zr the main key for your support and do you believe that MOFs can indeed be excellent candidates for catalysis that can address the industry needs?

Wenbin Lin responded: Yes to both questions!

Laura Gagliardi enquired: What is the oxidation state of Fe and how does it vary in the reactions that you considered? Did you do any further atomic or molecular characterisation of the process? Can you elaborate on that?

Wenbin Lin answered: For the precatalysts, we know for sure that Fe is in the +2 oxidation state.

Laura Gagliardi asked: Is iron a better catalyst than cobalt or not? And can you explain why in terms of the electronic structure or steric effects?

Wenbin Lin replied: The answer would depend on the reaction itself. Fe is better than Co in some reactions while Co is better in other reactions. One cannot generalize which one is better.

Timothy Easun commented: What is the best way to determine that catalysis is occurring within the framework rather than at potentially reactive sites on the crystallite surfaces?

Wenbin Lin answered: There are a number of experiments one can do to prove that catalysis is happening in the interior of a MOF. First, one can use substrates of very different sizes to test size-dependent conversions. This kind of test has been used since 2005.¹ Second, one can try to selectively poison the active sites on the surface to see if the catalytic activity is totally lost. Third, one should always look at the turnover number (TON). If the TON is small, the chance of surface catalysis only is high.

1 C.-D. Wu, A. Hu, L. Zhang and W. Lin, *J. Am. Chem. Soc.*, 2005, **127**, 8940–8941.

Carlo Lamberti asked: From the point of view of synthesis, how is functionalization achieved for mPT-MOF FeBr₂? Do you use FeBr₂-pre-functionalised ligands or you are you grafting FeBr₂ on the already crystalline MOF?

Wenbin Lin replied: Yes, we treated the MOFs built from the functional ligands with metal salts to generate the precatalysts.

Nathaniel Rosi commented: You've done a lot of work on this UiO family. How much work has been done to distinguish whether catalysis occurs in the octahedral cavity *versus* the tetrahedral cavity? It would seem that you could observe cavity size/geometry effects on product selectivity, *etc.*

Wenbin Lin replied: It would be difficult to differentiate the reactivities in tetrahedral *vs.* octahedral cavities because they are connected to each other.

Mohamed Eddaoudi asked: Can you elaborate on how your "SBU" polynuclear cluster in your material is different from the hexanuclear cluster (12-connected SBU) in the parent UiO-66? Is the SBU 8-connected or 6-connected? How many metal centers were added in addition to the six Zr metals in the original cluster?

Wenbin Lin responded: In the past couple of years, we have used Zr₆, Zr₈, and Zr₁₂ SBUs to design MOF catalysts. They lead to very different catalysts with vastly different reactivities.

Omar Farha asked: You are adding the metal postsynthetically, is this correct? How do you distinguish whether the metal goes into the linker *versus* the defect sites on the node?

Wenbin Lin answered: In the metal loading approach used in this paper, metal salts tend to favor coordination to bipy or phen.

Mircea Dincă said: In terms of commodity chemicals, what is your dream substrate for benzylic amination?

Wenbin Lin responded: The benzylic amination method would not be useful for making commodity chemicals due to the costs of the reagents. However, the method would be useful for making high value fine chemicals.

Frederik Haase commented: In your paper you showed the incorporation of the catalyst into the linker backbone of the MOF. In this case you would want to avoid catalytic activity from, for example, a Lewis acidic node. Have you seen cooperative catalysis or side reactions resulting from the nodes? Do you use nodes that are non-reactive by design?

Wenbin Lin responded: The reactions we chose for this work cannot be catalyzed by the metal nodes. Yes, one can use the active sites on the ligands and SBUs for cooperative catalysis. We published the first one previously.¹

1 F. Song, C. Wang and W. Lin, *Chem. Commun.*, 2011, **47**, 8256–8258.

Gareth Lloyd addressed Wenbin Lin: All conversations appear to come back to why are MOFs/porous materials useful, rather than the understanding we have obtained through a piece of scientific research. Are we aiming for understanding, or are we aiming for commercial use? Aren't we not more interested in scientific understanding first, and commercialisation second?

Wenbin Lin replied: We are trying hard to understand the fundamental science but at the end of the day, if our research (*i.e.*, the broader community) cannot lead to innovative products that will benefit society, our research cannot be sustained. So both fundamental understanding and practical applications are important in my opinion.

Ross Forgan commented: For a number of systems wherein homogeneous catalysts are supported on heterogeneous substrates, “boomerang catalysis” occurs, where the metal dissociates from the support to facilitate the catalytic reaction and is then bound again afterwards. Is this an issue in MOF catalysis, and is it truly heterogeneous?

Wenbin Lin responded: This is an interesting question. I would say that it can definitely happen, but in some of our recent reports, we are very confident about the “heterogeneous” nature of MOF catalysts. In fact, many MOF catalysts are “heterogeneous.”

Susumu Kitagawa commented: According to my experience in synthesis of organic polymers in the channels of a MOF, the size of a crystal in this catalytic reaction is important, as well as the defects in a crystal. Have you seen any effects that the length of the channels namely, a size of crystal, affect the activity of the MOF? Is it possible to do reactions in nanoscopic, mesoscopic, and macroscopic size of crystals?

Wenbin Lin responded: Yes, we see this phenomenon all the time. The reaction rate is very much dependent on channel sizes and the sizes of MOF crystals. We have published a perspective article to discuss this issue.¹

1 C. Wang, M. Zheng and W. Lin, *J. Phys. Chem. Lett.*, 2011, 2, 1701–1709.

Marco Ranocchiari opened a general discussion of the paper by Shengqian Ma: You justified your work by saying that this could be used for biomass conversion. You have a water phase system, and lignin or any biomass is not soluble in water. Plus you have an insoluble MOF. How do you foresee using MOFs for real biomass conversion?

Shengqian Ma responded: The current work is a “proof-of-concept” study, and there is still a long way to go for using MOFs for real biomass conversion before the cost and long-term stability issues of MOFs are resolved. In addition, for real biomass conversion, fixed-bed reactors are used, and more studies along this line should be conducted using MOF catalysts.

Jeffrey Paulo H. Perez asked: Based on the TEM images shown in Fig. 2(a) and (b) in your paper (DOI: c7fd00015d), you suggested that the Pd NPs are distributed in the cages of MIL-101 and MIL-101-SO₃Na. Did you use other high-resolution microscopy techniques such as electron tomography to confirm the presence of Pd NPs in the framework of the host material? I also noticed in Fig. 4 that there was a slight decrease in the yield of 2-methoxy-4-methylphenol in the recycling

tests, did you check for possible leaching of Pd NPs during catalysis by means of ICP analysis?

Shengqian Ma answered: We did not use electron tomography to confirm the presence of Pd NPs in the framework of the MOF. ICP-MS analysis did not indicate the leaching of Pd NPs during catalysis.

Jeffrey Paulo H. Perez continued: In my opinion, the TEM images shown in Fig. 2(a) and (b) do not clearly indicate that the Pd NPs are encapsulated in the cages of MIL-101 and MIL-101-SO₃Na. I strongly suggest to use annular-dark field scanning transmission electron microscopy (ADF-STEM) and electron tomography to elucidate the location of the Pd NPs in the host framework. A recent paper from our group showed that ADF-STEM and electron tomography are powerful nanoscale characterization tools to confirm the embedding of Pt NPs in MIL-101.¹

1. M. Meledina, S. Turner, M. Filippousi, K. Leus, I. Lobato, R. K. Ramachandran, J. Dendooven, C. Detavernier, P. Van Der Voort and G. Van Tendeloo, *Part. Part. Syst. Charact.*, 2016, **33**, 382–387.

Shengqian Ma answered: Thanks for the suggestion.

Mircea Dincă asked: There are catalysts that take ligands through challenging processes into other intermediates. Have you considered combining the catalyst with lignin conversion catalysts to see whether they can work in combination?

Shengqian Ma responded: It would be very challenging given that lignin conversion usually requires high temperature (>500 °C) but most MOF catalysts cannot survive above temperatures of 400 °C. Even if certain high-thermally stable MOF catalysts could be developed for lignin conversion, the efficiency would be low since the contact between the solid lignin substrate and active sites within the MOF catalyst is minimal. Nonetheless, a specific reactor system can be designed to combine a catalyst capable of degrading lignin with a MOF catalyst capable of upgrading the biofuel to achieve overall high efficiency.

Francesco Carraro asked: Do you think that the distance between the surface of the MOF crystals and the particle is crucial for the effectiveness of the catalysis? Pd is currently randomly dispersed inside and on the surface of the MOF crystal. Do you think that it might be interesting to grow shells of the MOF with different thickness around Pd NPs? This could permit to finely investigate the role of pores with different hydrophilicity on the catalytic properties of the material, without the contribution that could derive from a different dispersion of the Pd NPs in the investigated samples.

Shengqian Ma responded: These are very good suggestions.

Mohamed Eddaoudi said: How big are the resultant particles? How did you assess that the particles formed inside the cavities?

Shengqian Ma responded: The resultant particles are 2.5 nm and they were assessed *via* TEM.

Valeska Ting queried: What is the advantage of using a MOF as a nanoparticle support in this case, since you would expect that having your active nanoparticle confined inside a MOF pore of similar dimensions would limit the access of reactants to the reactive nanoparticle surface?

Shengqian Ma replied: MOFs can provide a tunable environment (*e.g.* hydrophobic/hydrophilic as in our paper, or chiral) within the vicinity of nanoparticle when it serves as the support. Since the loading of nanoparticle within MOF is usually low (<3%), the reactants can access the reactive nanoparticle surface from the windows of adjacent cages.

Pascal Van Der Voort asked: Would it be a fair statement to say that the main role of a MOF that contains nanoparticles is to keep them from aggregating and to keep them dispersed? If you've not done tomography, how do you know whether leaching or aggregation has occurred and whether they are actually inside the cages? An alternative approach could be to look at the used catalysts and to check whether or not the nanoparticles have grown. Did you try this?

Shengqian Ma answered: The absence of leaching of Pd nanoparticles was confirmed by ICP-MS studies after catalysis. The TEM studies on the used catalysts did not indicate the aggregation of nanoparticles.

David Harris opened a general discussion of the paper by Matthew Rosseinsky: You mentioned that with aluminium, it is much more stable because of the higher bond enthalpy, and with indium it is the reverse. What about gallium – is it difficult to get gallium single crystals?

Matthew Rosseinsky replied: In general, aluminium is uniquely difficult to access crystals from in this kind of chemistry. Gallium and indium are easier. We've taken advantage of the synthesis of isostructural materials in this project.

Valeska Ting asked: With these exotic flexible MOFs, characterisation is a real challenge if you don't have single crystal data. Can you comment on (perhaps non-standard) characterisation techniques that could be applied to these types of systems?

Matthew Rosseinsky replied: This is an important point to appreciate – you have to know the structure to understand the properties and, in flexible systems, the structure will, of course, change depending on the amount and nature of the guest species in the pores. Solution from powders is possible but challenging, so we go to considerable lengths to make crystals, and this is why the isostructural synthesis approach is used. There are many other non-diffraction techniques which are available and very useful, but crystallography forms the basis of understanding.

Aron Walsh asked: Indium oxide is a very effective bulk electron conductor. Do you have any evidence that the 1D indium oxide channels could support electrical conductivity?

Matthew Rosseinsky responded: This is an interesting idea. We would need to introduce defects that produce the n-type charge carriers, and we haven't managed to control the defect chemistry in this way. Getting control of defect chemistry is an interesting direction for MOF research.

Omar M. Yaghi commented: One of my students tried indium oxide and it didn't work!

Ross Forgan asked: Considering the number of hydrogen bond donors and acceptors in the ligands, can you comment on whether inter-ligand hydrogen bonding or ligand conformation would be the main structure directing force during self-assembly of these MOFs?

Matthew Rosseinsky replied: We would need to do computational studies to understand this in sufficient detail to answer your question – you are right to point out that both effects can be important.

Omar M. Yaghi said: Regarding the structures with the methanol complex in the pores – are they selective to methanol if there are other molecules present with the potential for hydrogen bonding? Is the structure templated by methanol, or is it tolerant?

Matthew Rosseinsky answered: I had not really thought about templating and selectivity, we should look at this point.

Omar M. Yaghi asked: This is a move towards the way people make zeolites, *i.e.* in terms of flexibility of angles. We don't have Si–O–Si but we have a flexible linker that could be templated by methanol. Unlike rigid MOFs where rigidity controls the structure, in your system you might have a templated response within the system that you could use for strategies as in zeolites.

Matthew Rosseinsky replied: This combination of flexibility, heavy chemical functionalisation and templating is an interesting direction to take the field. At this stage, we just don't understand enough about how such complex systems respond to guests, and this understanding will open up the sort of distinctive research directions that the question implies.

Omar M. Yaghi commented: Regarding the cyclability of the collapsed and expanded form, Jeffrey Long/Susumu Kitagawa can cycle many cycles, can you cycle that many times?

Matthew Rosseinsky responded: We have not studied this.

Carlo Lamberti opened a general discussion of the paper by Karena W. Chapman: If I understood correctly your results, you have been able to

simultaneously detect, and speciate, both small and big copper particles in the same sample, is this correct? If yes that's impressive and means that, for this specific case, the pair distribution function (PDF) technique can be much more informative than EXAFS, which would provide values averaged over the bimodal particle distribution.¹

1 G. Agostini, L. Bertinetti, A. Piovano, R. Pellegrini, G. Leofanti, E. Groppo and C. Lamberti, *J. Phys. Chem. C*, 2014, **118**, 4085–4094.

Karena Chapman answered: It is true, that in the PDF we can distinguish and quantify two populations of copper nanoparticles with different sizes. We can see this because the PDF includes the atom–atom correlations over large length scales, in contrast to EXAFS which is more short-sighted. At large distances in the PDF, only the contributions from the large nanoparticles are observed and can be reliably modeled. We can then constrain this component when modeling the data to low r where the contribution from the small nanoparticles becomes apparent. In the same way, we can distinguish amorphous phases in the presence of more ordered crystalline or nanoscale phases. Small-angle scattering data could be used to quantify the distribution in particle sizes, particularly for more complex size distributions.

Carlo Lamberti asked: In your experience in the characterization of MOFs with synchrotron radiation techniques, did you face problems with sample damage from intense and focused X-ray beams?

Karena Chapman responded: It is important to be aware that interactions of X-rays with a sample can influence its structure and function. Such “beam damage” will scale with X-ray absorption and will, therefore, be of greatest concern for measurements using low energy X-rays and X-ray energies close to the absorption edge of elements within the sample (*i.e.* energies relevant to X-ray absorption studies). For our PDF measurements and the present MOF characterization, we use high energy X-rays (wavelengths of ~ 0.2 Å) that are highly penetrating. At high X-ray energies, there is no significant X-ray absorption by the sample and, hence, beam damage is minimised.

Pascal Van Der Voort asked: You mentioned that the copper ions can move up to 100 nm to grow nanoparticles that are slightly bigger than the host cage. Can you exclude the possibility that the nanoparticles span multiple cages?

Karena Chapman replied: The Cu species move, likely as reduced Cu⁰, to form nanoparticles that are several Ångströms larger than what we consider to be the diameter of the channels within the NU-1000 MOF. However, this channel dimension is based on the most confined aperture along the channel. There are wider apertures along the channel that I imagine could accommodate the 4 nm nanoparticles. As you suggest, there is a possibility that nanoparticles can span multiple channels, as has been seen in other MOFs. However, in my mind, if nanoparticles were not confined by the framework pores and could span multiple channels they would be expected to continue to grow with time. This is contrary to our observation that once formed, the Cu nanoparticles do not grow, hence, our

conclusion that the nanoparticles are confined within the individual pores of the NU-1000 framework.

Pascal Van Der Voort continued: To follow up on the previous question, have you performed TEM measurements to visualize the nanoparticles?

Karena Chapman responded: We have not performed TEM on this specific system. If we were to do so, we would need to take care to employ low dose measurement strategies as exposure to the electron beam itself can lead to changes in the sample structure and induce nanoparticle formation in MOFs.

Jing Li asked: In addition to estimating the particle size of copper nanoparticles, you mentioned that the PDF analysis may be capable of distinguishing particles that are inside the pores and on the surface. What bonding information is used to tell such a difference?

Karena Chapman responded: We directly locate species within the pores of the crystalline lattice using the difference envelope density (DED) analysis rather than the PDF data. The DED provides us with a low resolution map of where the electron density in the pore changes during the reaction. From PDF alone, we are generally only indirectly sensitive to the location of the nanoparticles, with this information being inferred from the size of the particles and how this evolves with time.

Lauren McHugh said: Have you tried a technique such as EDX elemental mapping to observe copper within the MOF pores?

Karena Chapman responded: We have not undertaken EDX on this specific system, but it has been done for other metal species deposited in this MOF using the same atomic layer deposition (ALD) approach. While the resolution of the EDX has been insufficient to directly visualise the metal species within the pores, it does suggest that the species are uniformly distributed throughout the MOF crystals.

Mircea Dincă asked: Regarding the ion or metal atom mobility in MOFs, how does it compare to the surfaces of other materials, porous or not? In the copper example described here, do you see any evidence for copper ions, rather than atoms, being mobile? If you estimate 100nm mobility, how does that compare to, for example, a zeolite?

Karena Chapman answered: Compared to previous systems I've studied, I would say that the Cu mobility in NU-1000 is quite high. At the 10 min time resolution of the measurement, we only see the final nanoparticle size and not the preceding growth. We don't have direct evidence as to whether the species moving are in the cationic or reduced state. I suspect it is the reduced Cu atoms as I'd expect cations to be strongly bound within the Cu-oxo clusters. The 100 nm reflects the minimum distance over which Cu atoms would need to migrate to form 4nm nanoparticles, based on the original density of Cu within the NU-1000.

The distance over which they migrate could be larger. Depending on the zeolite, I've seen evidence for mobility over similar length scales.

Aron Walsh commented: There have been reports of atomic layer deposition achieving atomic control of ion distribution in MOFs. Such a process requires self-limiting growth. Your experiments appear to suggest that even before annealing, clusters of several Cu atoms are present in a range of local environments. If the initial aim was a single Cu species attached to an OH group in the MOF, does this suggest a limitation of ALD in MOFs?

Karena Chapman replied: We do see that ALD reactions in MOFs are self-limiting – in this system a maximum of 4 Cu are reacted per Zr_6 node. However, our experiments to date suggest that there is much to learn about how ALD processes occur in MOFs. The pore surface in MOFs is very different from conventional ALD substrates. The MOF surface is not locally planar. The pores have large aspect ratios, complex architectures, heterogeneous surface chemistry and similar dimensions to the organometallic ALD precursors which presumably must adsorb within the MOF before reacting. Once we develop a better understanding of how the ALD processes applies to MOFs, I imagine that we will be able to achieve more precise control of the ion distribution.

Jane Knichal remarked: Is there the possibility to expand this research to other metals, for example to make gold nanoclusters/nanoparticles?

Karena Chapman responded: The approaches that we have used in the present system can be applied to a broad range of other metal species, including gold. Indeed we have plans to study the gold analogue in the coming weeks.

Pascal Van Der Voort said: You talked about surfaces being sticky or slippery in terms of ion-transport. What is your definition of “sticky”? Is it quantifiable in any way? Can you write a formula for it that defines it?

Karena Chapman answered: I find it useful to think about surfaces being “sticky” or “slippery” when considering the mobility of species adsorbed on the surface and how readily these migrate and aggregate as larger metal nanoparticles. In this respect alumina would be “sticky” while silica would be “slippery”. In probing the mechanism and kinetics for nanoparticle growth, we often include a rate constant that accounts for the diffusion step (see, for example, ref. 1); in this way we would quantify the energetics and rates relevant to diffusion and, hence, the “stickiness” of the surface.

1 H. Zhao, T. M. Nenoff, G. Jennings, P. J. Chupas and K. W. Chapman, *J. Phys. Chem. Lett.*, 2011, 2, 2742–2746.

Marco Ranocchiari opened a general discussion of the paper by Jeffrey R. Long: About the confinement effect, you are using the UiO-67 system hoping to observe smaller oligomers in your catalysis. Farrusseng and Canivet have reported dimerisation with similar nickel complexes using MIL-101 with significantly larger pores and much higher selectivity to the dimer.¹ Is it really confinement

that plays a role in this reaction? Do you think that the enhanced selectivity might be caused by how the metal is dispersed throughout the MOF?

1 J. Canivet, S. Aguado, Y. Schuurman and D. Farrusseng, *J. Am. Chem. Soc.*, 2013, **135**, 4195–4198.

Jeffrey Long answered: Selective dimerization of ethylene to butene can be achieved if the rate of chain termination greatly exceeds the rate of chain propagation, while a Schulz–Flory distribution of oligomers is produced if the rates of these two reactions are similar. For molecular systems, the metal coordination environment of the catalyst can be tuned to favor ethylene dimerization over a Schulz–Flory distribution of oligomers. In the paper by Farrusseng and Canivet, it is likely that the coordination environment controls the catalyst selectivity. We decided to study systems based on Ni-bipyridine catalysts specifically because analogous molecular systems have been shown to give a Schulz–Flory distribution of oligomers. Confinement effects would be easier to identify in these systems as it would be unusual for deviations from the Schulz–Flory distribution to arise from the influence of the immediate coordination environment.

To answer your second question, the dispersion of the active nickel sites does result in enhanced selectivity for oligomers over polymers. As we discuss in the paper, relieving the steric environment around the nickel sites can lead to an increased rate of chain termination over chain propagation, favoring the formation of oligomers over polymers. We don't think active site dispersion can account for the deviation from the Schulz–Flory distribution apart from facilitating the activation of more nickel sites within the crystal interior, which we believe to be influenced by framework confinement effects.

Marco Ranocchiari commented: Have you characterized the catalyst that forms polymers after the reaction? Sorption properties after catalysis will confirm if the pores are blocked by polymers.

Jeffrey Long replied: Besides showing that highly crystalline polyethylene is formed, we have not done further characterization of the polymers obtained from the reaction.

That is a good suggestion. In addition to characterizing the gas sorption properties, catalyst recycling experiments and monitoring the rate of the reaction over an extended period should also help determine if pore blockage can become a potential problem over time. What we would really want is to design catalysts that do not make any polymer at all, which would lessen the amount of ethylene converted to unwanted side products and avoid potential issues arising from reactor fouling.

David Harris asked: What are the design principles for catalysts for ethylene oligomerisation? Do you need open coordination sites? Why do you use nickel, what's good about nickel?

Jeffrey Long responded: There are two main classes of ethylene oligomerization catalyst: those that proceed through the Cossee–Arlman mechanism, which either selectively dimerize ethylene or give a Schulz–Flory distribution of

oligomers, and those that follow the metallacycle mechanism, which can selectively form trimers or tetramers. We have initially focused on developing heterogeneous catalysts inspired by Ni-based molecular systems that have generally been shown to function through the Cossee–Arlman mechanism. For these systems, catalyst selectivity is dictated by the relative rates of chain termination and chain propagation. Catalysts that have much faster rates of chain termination produce butene selectively, as demonstrated in Mircea Dincă's work.^{1,2} In systems with comparable rates of chain termination and propagation, such as the catalyst used in the Shell Higher Olefin Process³ and those studied by Brookhart,^{4,5} a Schulz–Flory distribution of oligomers is produced. If chain propagation is much faster than chain termination, however, the catalyst becomes an ethylene polymerization catalyst. Among other things, the steric environment around the metal center has been used to control the relative rates of these two reactions. Placing steric bulk near the axial sites of the metal retards chain termination by hindering the associative substitution of the oligomer chain by ethylene. Brookhart has leveraged this strategy to design ethylene polymerization catalysts derived from ligand scaffolds that only give oligomers.⁶ Conversely, promoting chain termination by relieving the steric environment around the metal center can result in catalysts that either dimerize ethylene or produce a Schulz–Flory distribution of oligomers.

For catalysts operating through the Cossee–Arlman mechanism, at least three accessible coordination sites are necessary. In the chain termination step, β -H elimination results in two sites being occupied by a coordinated olefin and a hydride. A third site is required for ethylene to bind and displace the existing olefin chain through associative substitution.

With the goal of investigating pore environment effects on ethylene oligomerization, it was critical for us to find systems that give a predictable distribution of oligomers encompassing chain lengths that would be more likely to be influenced by confinement within the framework pores. We anticipated that this would help us distinguish between effects that could be attributed to the structure of the catalyst around the metal center and those that might arise from enclosing the active site within the pores of a metal–organic framework. For example, it is difficult to determine if confinement effects are operative in systems that selectively dimerize ethylene because such selectivity can be readily achieved by tuning the coordination environment in molecular catalysts. We also surmised that catalysts producing a broad range of oligomer chain lengths would be required to access intermediates with chain lengths long enough to be affected by pore confinement. Thus, we chose to study systems that would give a Schulz–Flory distribution of oligomers. While oligomerization catalysts based on other metals, such as Fe, have also been reported to give this product distribution, we specifically pursued Ni-based systems because these are by far the most extensively studied and understood. In addition, Ni-based systems have been shown to have low barriers to insertion, which controls the overall catalyst activity in these systems, and associative displacement of the oligomer chain, which favors the formation of oligomers over polymers.

1 E. D. Metzger, C. K. Brozek, R. J. Comito and M. Dincă, *ACS Cent. Sci.*, 2016, **2**, 148–153.

2 E. D. Metzger, R. J. Comito, C. H. Hendon and M. Dincă, *J. Am. Chem. Soc.*, 2017, **139**, 757–762.

3 W. Keim, *Angew. Chem., Int. Ed.*, 2013, **52**, 12492–12496.

- 4 C. M. Killian, L. K. Johnson and M. Brookhart, *Organometallics*, 1997, **16**, 2005–2007.
5 S. A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65–74.
6 L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414–6415.

Connie Lu commented: The catalytic activity of the control material, where Ni is added to the biphenyl-MOF, is fascinating because it emulates the product distribution and the turnover frequency (TOF) for the second material almost exactly, whereas the Ni loading is 8-fold less. Do you observe Ni leaching into solution for the control? If the Ni is stable inside the material, what is the coordination environment of the Ni center?

Jeffrey Long responded: I agree, we were also surprised by the similarity in product distribution between the control and the material with dispersed bipyridine sites. While the similar selectivities could be the result of the confinement of both sites within the framework pores, the likely presence of two different active sites in the bipyridine-functionalized materials prevents us from concluding that this behavior arises from confinement effects. Evaluating the selectivity of expanded analogues of both materials would help distinguish between the effects of framework confinement and the presence of two different active sites.

At the low Ni loadings we obtain for the biphenyl control and the material with dispersed bipyridine sites, we don't expect the Ni loading to have significant effects on the TOF, which is normalized to the amount of Ni in the material.

We have not attempted to quantify the amount of Ni leached after the control reaction. The Ni in the biphenyl framework is retained after several dimethoxyethane washes at 80 °C, suggesting that these species are tightly bound. While we have not characterized the coordination environment of the Ni species, we believe that they are coordinated by water and hydroxide ligands that occupy vacant linker sites on the Zr cluster. Hong-Cai Zhou's group has crystallographically characterized Ni binding to these sites in a metal-organic framework with the same Zr cluster but a different topology.¹

1 S. Yuan, Y.-P. Chen, J. Qin, W. Lu, X. Wang, Q. Zhang, M. Bosch, T.-F. Liu, X. Lian and H.-C. Zhou, *Angew. Chem.*, 2015, **127**, 14909–14913.

Connie Lu continued: This is a follow up question. Can you use the Ni-loading as a method of measuring/probing defect sites?

Jeffrey Long answered: While we haven't made any direct efforts to correlate the amount of linker vacancies to the Ni loading, it would be interesting to see if Ni selectively binds to all the vacant linker sites on the Zr cluster.

Mircea Dincă said: Regarding the deviation from the Flory–Schulz distribution: If you have diffusion effects, as others have suggested, you should see potential octene products from the dimerization of butene, which should diffuse slowly in the pores. Do you see any evidence that the catalyst is active for the dimerization of larger olefins, and if so, have you looked at the potential formation of branched octenes from any undesired butene dimerization?

Jeffrey Long answered: While we haven't specifically looked for branched octene products in the reaction mixture, we have conducted preliminary experiments that indicate that the catalyst has some activity for the dimerization of larger olefins. Running the ethylene oligomerization reaction in neat 1-octene as the solvent gives a product distribution in which the amount of hexadecene is slightly greater than what would be expected from the Schulz–Flory distribution. We attribute the additional hexadecene to the dimerization of solvent 1-octene. The amount of hexadecene contributed by dimerization, however, is much less than that produced from the oligomerization, even if the concentration of 1-octene is much higher than that of ethylene. These results suggest that the dimerization of larger olefins occurs at much slower rates compared to ethylene oligomerization, which is consistent with analogous ethylene oligomerization catalysts.¹

1 S. A. Svejda and M. Brookhart, *Organometallics*, 1999, **18**, 65–74.

Omar Farha commented: We see that nickel goes into defect sites.

Carlo Lamberti remarked: In your work, you succeeded in inserting almost 100% functionalized linkers, is this right?

Jeffrey Long answered: Yes, we see complete metalation of the bipyridine linkers in the microcrystalline powder sample by ICP-OES analysis and in the single crystals based on refinement of the Ni occupancy at the bipyridine sites in the single crystal structure.

Wenbin Lin remarked: I am curious whether you have thought about using better defined activators? My suspicion is that trapped NiCl might be activated.

Jeffrey Long answered: We selected diethylaluminum chloride (Et_2AlCl) as a much more well-defined activator in comparison to methylaluminoxane (MAO), which is a more typical activator for ethylene oligomerization and polymerization catalysts. In addition, Et_2AlCl would be able to reach more of the bipyridine– NiBr_2 complexes within the framework due to its smaller size compared to MAO. As we mention in the paper, we believe that dispersion of the nickel(II) sites in the framework increases their accessibility to the Et_2AlCl , resulting in the higher TOF observed in the material with bipyridine–nickel complexes at only a fraction of the linkers.

Wenbin Lin asked: Regarding defects: we probably don't know what is happening with the defects. You could quantify this by looking at the ratio between the metal and the ligand.

Jeffrey Long replied: I agree. In metal–organic frameworks that rely on the functionalization of defect sites for catalysis, it would be very helpful to quantify the amount of defect sites present in the material.

Karen Leus remarked: Based on the earlier question from Connie Lu, it is clear from Table 2 in your paper (DOI: c7fd00061h) that the Ni complex embedded in

the biphenyl UiO-67 also exhibits good catalytic performance in the oligomerization of ethylene in comparison to the anchored complex in the bipyridine UiO-67. Which material exhibited the best results in term of recyclability and stability?

Jeffrey Long replied: As the initial focus of our study was to probe for pore environment effects on ethylene oligomerization, we have not evaluated any of the materials for recyclability or stability.

Karen Leus remarked: It is well known that bipyridine moieties are good anchoring points to stabilize several metal complexes. After anchoring the Ni complex in the UiO-67 materials, which framework exhibited the highest amount of Ni leaching, the biphenyl or bipyridine-based UiO-67?

Jeffrey Long answered: We have not made any attempts to quantify Ni leaching from the oligomerization reaction mixtures; however, no additional product formation was observed after the solid bipyridine-based catalysts were removed from the reaction mixture by filtration. In addition, all the Ni-treated materials still contained Ni after being washed three times with dimethoxyethane at 80 °C, suggesting that the nickel species in these materials are tightly bound. Considering that the oligomerization reactions were performed in cyclohexane, it is unlikely that leaching of significant amounts of Ni occurred during the reactions, though we cannot rule out that leaching may arise from the formation of catalytically inactive cyclohexane-soluble nickel species.

Carlo Lamberti commented: Cr(IV) grafted on silica (Phillips catalyst¹) is an industrially used catalyst for ethylene polymerization, but also the Cr(II)/silica (obtained by reducing the Cr(VI)/silica system in CO at 350 °C) is very active.² A Cr(II) MOF, already synthesized in Long's group,³ may also be active, and may result in oligomerization catalysis owing to the steric hindrance of the MOF cavities, as observed when the reaction is performed inside a zeolitic framework.⁴ In this regard, very recently, it has been reported that MIL-100(Cr) MOF displayed high selectivity to low carbon olefin products (C₆, C₈, C₁₀) and moderate catalytic activities.⁵

1 M. P. McDaniel, *Adv. Catal.*, 2010, **53**, 123–606.

2 E. Groppo, C. Lamberti, S. Bordiga, G. Spoto and A. Zecchina, *Chem. Rev.*, 2005, **105**, 115–187.

3 L. J. Murray, M. Dincă, J. Yano, S. Chavan, S. Bordiga, C. M. Brown and J. R. Long, *J. Am. Chem. Soc.*, 2010, **132**, 7856–7857.

4 C. Lamberti, E. Groppo, G. Spoto, S. Bordiga and A. Zecchina, *Adv. Catal.*, 2007, **51**, 1–74.

5 S. Liu, Y. Zhang, Y. Han, G. Feng, F. Gao, H. Wang and P. Qiu, *Organometallics*, 2017, **36**, 632–638.

Omar Farha asked: Jeff wants to make to shorter oligomers than polymers.

Wenbin Lin asked: Might it be possible to think about poisoning of the outer surface sites? This may be able to shut down polymerisation.

Jeffrey Long replied: This is a good suggestion. We have conducted several preliminary experiments in this direction and do see reduction in polymerization

activity relative to oligomerization in materials treated to poison or inactivate the surface sites.

Frederik Haase asked: Have you investigated the particle size of your MOF catalyst and do you see a size or external surface area effect on catalytic activity, especially with regard to side reactions? If no size effect is visible, would this be an argument against the external surface of the MOF being catalytically active?

Jeffrey Long answered: We have not looked into particle size effects; however, preliminary experiments show that there is less polymer formation under conditions meant to selectively poison or inactivate the surface Ni sites. These results suggest that sites on the external surface of the framework are likely the major source of polyethylene produced during the reaction.

Aron Walsh asked: Unfortunately, there have been no contributions on magnetism at this Faraday Discussion. I would like to ask one general question drawing from your expertise on this topic. Achieving robust room temperature magnetic order in MOFs remains a grand challenge. However, an advantage of MOFs over denser crystals is the regular array of isolated metal (spin) centres. Could you see MOFs being used for quantum information in the future, or do you see other directions in the field of magnetic MOFs?

Jeffrey Long answered: Metal–organic frameworks with nodes that are also single-molecule magnets can indeed serve as powerful platforms for testing the effects of how the spatial relationship between such species impacts slow magnetic relaxation, as well as how contact with adsorbed guest molecules may alter their magnetic behavior.¹ Additionally, ongoing research in other laboratories is seeking to achieve quantum sensing using frameworks of this type that feature an array of nodes with long coherence times.² The synthesis of metal–organic frameworks exhibiting magnetic ordering at high temperatures remains an open challenge, which if met could lead to new light-weight magnets and perhaps even porous materials capable of performing magnetic separations, such as in the separation of O₂ from air.

1 X. Zhang, V. Vieru, X. Feng, J.-L. Liu, Z. Zhang, B. Na, W. Shi, B.-W. Wang, A. K. Powell, L. F. Chibotaru, S. Gao, P. Cheng and J. R. Long, *Angew. Chem., Int. Ed.*, 2015, **54**, 9861–9865.

2 J. M. Zadrozny, A. T. Gallagher, T. D. Harris and D. E. Freedman, *J. Am. Chem. Soc.*, 2017, **139**, 7089–7094.

Zhijie Chen opened a general discussion of the paper by Susumu Kitagawa: My question is about the memory effect. In one of your slides, you showed that the energy difference between the closed pore state and open pore state and the transition between them can be achieved by applying the gas pressure or other triggered force.¹ My question is whether downsizing crystals is the only way to achieve a memory effect? Could you please comment?

For example, for a specific structure, gas molecules with higher interaction energy with the framework (*e.g.* CO₂, butane) can open and close the framework. However, gas molecules with less energetic interactions (*e.g.* CH₄, N₂) could open the structure but can not close the framework. Some molecules (*e.g.* CO₂, butane)

can cross the energy barrier of closing the structure but others (e.g. CH₄, N₂) can not, the structure keeps an open state.

1 F.-X. Coudert, M. Jeffroy, A. H. Fuchs, A. Boutin and C. Mellot-Draznieks, *J. Am. Chem. Soc.*, 2008, **130**, 14294–14302.

Susumu Kitagawa replied: For the first question, no, we have just found one example. As I mentioned in my talk, you have chances to find other phenomena, in which unique properties emerge upon controlling porous network parameters.

For the second question, molecules with strong interaction ability tend to open pore gates, while molecules with weak interaction ability can not. This is quite a normal phenomenon. Regarding the closure of a porous gate, the removal of guest molecules with strong interaction ability tends to induce a phase transformation. Your comment that CH₄ and N₂ keep an open state in spite of opening the gate, seems rare.

Matthew Ryder remarked: About your work on selective crystal growth and the control of crystal morphology *via* modulation or ‘capping’ of exposed facets, do you perceive that it is feasible for this area of research to eventually lead to particles being grown in a particular crystallographic orientation to take advantage of anisotropic properties such as mechanical (shear instabilities and auxeticity) and electrical (dielectric and piezoelectric) response? Moreover, if so is the limiting factor primarily due to the current lack of understanding surrounding the crystal growth and nucleation mechanisms?

Susumu Kitagawa answered: This is a very interesting and important issue to be addressed for the next decade. The coordination modulation method could be a useful one because of the chemical process. Based on this, various approaches to control crystal anisotropy would appear in conjunction with other methods.