

Mind the gap

Models play a significant role in the development of catalysts. However, they are constructed using a reductionist approach and this poses the question of their relevance for the comprehension of physical phenomenon.

A bridge is a powerful metaphor. It implicitly evokes the existence of a gap but at the same time imagines a means to fill it. Thanks to its immediacy and suggestive power, the image of a bridge has often been employed to indicate the possibility of connections within very different areas of the human knowledge. Catalysis — as a discipline featuring different subfields, areas of expertise and methodological approaches — is no exception.

In a previous issue, we recalled some areas of catalysis where gaps are being filled through the construction of bridges¹. As homogeneous, heterogeneous and biocatalyses are based on common physical principles we discussed, for example, how bridging between these sub-disciplines by targeting hybrid catalytic systems can in principle open new possibilities¹ — think, for instance, of the area of single metal atoms, which bridges homogenous and heterogeneous catalysis. There are cases however in which the possibility of constructing bridges has been more complicated. A long-standing conundrum in the catalysis community emerged at the interface between surface science and heterogeneous catalysis, better known as the pressure and materials gap.

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This problem was clearly defined during the 1980s, when significant progress was made in surface science in the determination of the gas sorption properties of single-crystal surfaces. Per Stoltze wrote in 1987, “From numerous studies of the adsorption of gases on single-crystal surfaces much has been learned on the kinetics, thermodynamics and structural aspects of chemisorption. It seems obvious that this very detailed information should be used as a basis for the understanding of heterogeneous catalysis”².

However, he continued, “For a number of reasons ... this is not straightforward”. In fact, surface science has been dominated by a number of techniques that provide reactivity data for reactions under ultra-high-vacuum conditions — pressures that are orders of magnitude different from actual catalytic reactors. The higher pressures render adsorbate–adsorbate interactions very important, and could, for example, lead to clear mechanistic differences.

Besides this pressure gap, the materials gap was further understood to be caused by the complexity and heterogeneity of real catalysts under applied conditions, as opposed to studies on single crystals. Certainly, in many cases, filling such gaps is not trivial. This is probably one of the reasons for the development of in situ catalysis studies, the importance of which was emphasized in this journal a few issues ago³. Using in situ studies means that direct information on a catalytic process is obtained, bypassing the use of models as well as the related necessary extrapolation of results to practical conditions. However, the level of insight that can be provided by in situ studies may be not sufficient alone to gain precise understanding of catalytic systems. Therefore, model studies, which provide powerful means for determining kinetic constants and reaction paths, should not be neglected. In fact, if the mechanistic aspects of the process are known in detail and remain consistent under a broad range of conditions, the gaps between single-crystal studies and realistic catalytic systems can be bridged. For instance, Stolze and Nørskov showed that in the case of ammonia synthesis, the kinetic information obtained via single-crystal studies in ultra-high vacuum could be extrapolated to industrially relevant conditions, allowing them to calculate the actual rate of reaction⁴.


Continuing in this tradition, in this issue Madix and colleagues [report a study](#) that reveals the remarkable predictive ability of single-crystal studies⁵. The authors investigate the oxidative coupling of methanol on nanoporous Ag_{0.03}Au_{0.97} and show how the kinetic information obtained on gold single crystals at low temperature (200 K) and vacuum ($\sim 10^{-5}$ bar) conditions allows prediction of the selectivity of the same process in a reactor operating at much

higher temperatures and pressures — 425 K and 1 bar. In this particular case, the correspondence between the model studies and the working catalytic system is ensured by a series of conditions that have been verified by the authors through previous experimental studies; the fact that the reaction is structure-insensitive and that the mechanism is preserved over a large temperature and pressure range is central to the success of this approach. In other words, the authors were able to confirm the accuracy of their model.

This brings us to a more general and interesting problem that has always kept philosophers of science busy: what is the correspondence between models and reality in science? Can this gap be bridged? Many areas of catalysis are permeated by this question. Consider for instance the computational tools that are increasingly being used in catalysis. More and more frequently, catalysis studies feature sections in which theoretical modelling is used to provide an interpretative framework for the observed experimental results, be these in the area of homogeneous, heterogeneous or bio-catalysis. Even more commonly, computations are being used to guide and influence the design of experiments a priori. Each computational study is, however, based on a model constructed according to reductionist criteria. And despite the success of modern computational catalysis — calculations are often at least qualitatively in good agreement with experimental findings — it is important to recall the importance of determining the accuracy of a model, as well as that of the method. In this regard, Evgeny Pidko recently reminded us that wrong models can provide right answers⁶. Determining the accuracy of a model becomes even more relevant as computational studies move away from the simulation of catalytic processes under single-crystal study conditions — 0 K, in vacuum — and target the evaluation of more-realistic systems, thereby attempting to close the temperature and pressure gaps in silico.

Verifying the accuracy of models can be a complicated task, and may require diverse expertise and knowledge from the catalysis repertoire. In many cases, such a level of expertise may go beyond the competences of single academic research

groups. Once again, the answer seems to be in the cooperation between the subfields of catalysis. Here, ironically, difficulties can arise as catalysis practitioners tend to speak different languages or use different jargons, or more generally have quite different mindsets. So perhaps the next gap to be

filled should be the one in communication. But this is another story, and shall be told another time. 

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References

1. *Nat. Catal.* **1**, 307 (2018).
2. Stoltze, P. *Phys. Scr.* **36**, 824 (1987).
3. *Nat. Catal.* **1**, 165–166 (2018).
4. Stoltze, P. & Nørskov, J. K. *Phys. Rev. Lett.* **55**, 2502 (1985).
5. Reece, C., Redekop, E. A., Karakalos, S., Friend, C. M. & Madix, R. J. *Nat. Catal.* <https://doi.org/10.1038/s41929-018-0167-5> (2018).
6. Pidko, E. A. *ACS Catal.* **7**, 4230–4234 (2017).