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# Mind the gaps in CO<sub>2</sub>-to-methanol

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## Standfirst

Catalyst structures dynamically respond to reactive atmospheres, often leading to intrinsically distinct active sites and reaction pathways when the reaction pressure is altered. This pressure gap and the degree of the gap are dependent on the nanostructure of catalysts. The gaps and discrepancies widely reported in *in situ* and *operando* studies of CO<sub>2</sub>-to-methanol using Cu-Zn catalysts have now been rationalised.

## Main Text

A catalyst is like a chameleon. It adopts in response to the surrounding environment. In the case of heterogenous catalysts, the chemical potential defined by the atmosphere and in particular the type of adsorbates (reactants, intermediates and products), their electronic nature and surface concentration can induce structural changes to the catalyst and thus to the nature of the catalytic active sites<sup>1,2</sup>. This effect is recognised as the pressure gap, often witnessed in the observed differences in reactivity measured under ultra-high vacuum (UHV) conditions using model catalysts and under technologically more relevant pressure conditions using technical and nano-structured catalysts<sup>3</sup>. Each catalyst structure, e.g. extended surfaces or (un)supported nanoparticles, responds distinctly to the reactive atmosphere, leading to material gaps when evaluated at the same pressure and temperature<sup>4</sup>. When these two factors are combined, the gap becomes very large and the obtained structural and mechanistic insights about the catalyst and active species or sites at low pressure may not be relevant to understand the activity observed with catalysts under a technologically relevant environment (Figure 1).

Many important catalytic processes are operated at high-pressure to benefit from the kinetic and thermodynamic advantages of such conditions to obtain products at high yields in a short reaction time and within a limited space. With the advent of advanced *in situ* and *operando* methodologies, nowadays more precise geometrical and electronic structures of catalysts and surface species can be elucidated in the lab and external facilities, e.g. using synchrotron light<sup>5,6</sup>. However, due to technical and sensitivity limitations given by the design of spectroscopic cells and measurement principles (e.g. electron detection), often the measurements are performed at lower pressure (<1 bar). The upper limit of measurement pressure of conventional vacuum techniques, such as X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM), is increasing to allow *in situ* and *operando* studies, but is typically limited to <50 mbar range. The pressure gap is often assumed negligible in mechanistic interpretations and the presence of unique meta-stable structures of catalyst materials under pressurised conditions is ignored.

Methanol synthesis by CO and CO<sub>2</sub> hydrogenation is an important catalytic reaction and the most famous and widely studied catalyst contains Cu and Zn as the active elements<sup>7</sup>. Due to the current and future importance of methanol produced from CO<sub>2</sub>, numerous researchers investigated the active sites through elucidation of Cu-Zn structures, their interactions and indicated reaction pathways. Despite thorough studies using model and technical catalysts, we can witness active debates over a few decades on the catalyst structures responsible for the unique activity due to the Cu-Zn synergy. Of the debated active Cu-Zn structures, there are three widely proposed ones, Cu-Zn alloy, Cu-Zn interface created between reduced Cu and ZnO nanoparticles and Cu-Zn interface created by ZnO overlayer on Cu nanoparticles.

Now, writing in *Nature Catalysis*, Willinger, van Bokhoven and co-workers shed light on the structures of an industrial Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst and how the Cu and Zn active elements respond dynamically to the pressures varying in 4 orders of magnitude (1 mbar – 10 bar) [ref. 8]. Precise catalyst structures in the wide range of pressure conditions were determined by *in situ* and *operando* X-ray absorption spectroscopy (XAS) under hydrogen during activation pretreatment and under the reaction mixture during CO<sub>2</sub> hydrogenation. Hydrogen pretreatment condition is known to play critical roles in defining the activity of Cu-Zn containing catalysts, and how the pretreatment conditions affect the structures of the Cu and Zn components and their interactions was clarified. Generally, it is challenging, if at all possible, to disentangle overlapping spectral contributions arising from different materials and their electronic structures observed in XAS. This was made possible by means of multivariate spectral analysis through kinetic resolution<sup>9</sup>, and the evolution of the structural composition during the studies could be precisely elucidated.

A unique combination of hydrogen pressure, temperature and duration of the reductive pretreatment led to the distinct structures and oxidation states of Cu, Zn and their mixture. The formation of Cu-Zn alloy over Cu particle through migration of Zn, often reported as the active site, was facilitated at higher reduction pressure above 100 mbar, more favourably at higher temperature. Building upon this precise information and understanding on the types of Cu and Zn containing structures after the hydrogen pretreatment, the structure of the catalyst under *operando* conditions was investigated at different pressure of the reaction mixture (CO<sub>2</sub> and H<sub>2</sub>). The structure underwent dynamic changes in response to the pressure of the reaction mixture. Most prominently, the Cu-Zn de-alloying was observed when the catalyst is highly active, i.e. at higher pressures, implying that the active sites under technically relevant conditions is not Cu-Zn alloy. The formation of ZnO overlayer<sup>10</sup>, or its absence, is suggested to be history dependent. Such an overlayer formation requires prior migration of Zn over Cu, like in the process of the Cu-Zn alloy formation. When the Zn of the Cu-Zn alloy formed over Cu particles is oxidised, the ZnO overlayer is formed. When such Cu-Zn alloy structures are not formed during the hydrogen pretreatment, the catalyst structure during the reaction would consequently contain no or little ZnO overlayer over Cu. This shows that the history of the catalyst matters to understand the actual structure and rationalise its activity.

The relevance and importance of *operando* and systematic studies are highlighted to bridge pressure gaps. This work clarified the origin of discrepancies reported in literature on the nature of the active sites and the roles of pressure gaps during pretreatment, reaction and spectroscopic studies. It is also important to note that the conclusion was drawn using the bulk sensitive technique and there is a possibility that surface structure of the catalyst may tell us an additional story. We may have just started to look at the one important side of the real complex yet beautiful catalysis. Without these precise experimental efforts, no true understanding of catalysis can be achieved and advancement in computational atomistic simulation of catalytic active sites is difficult.

## Competing interests

The author declares no competing interests.

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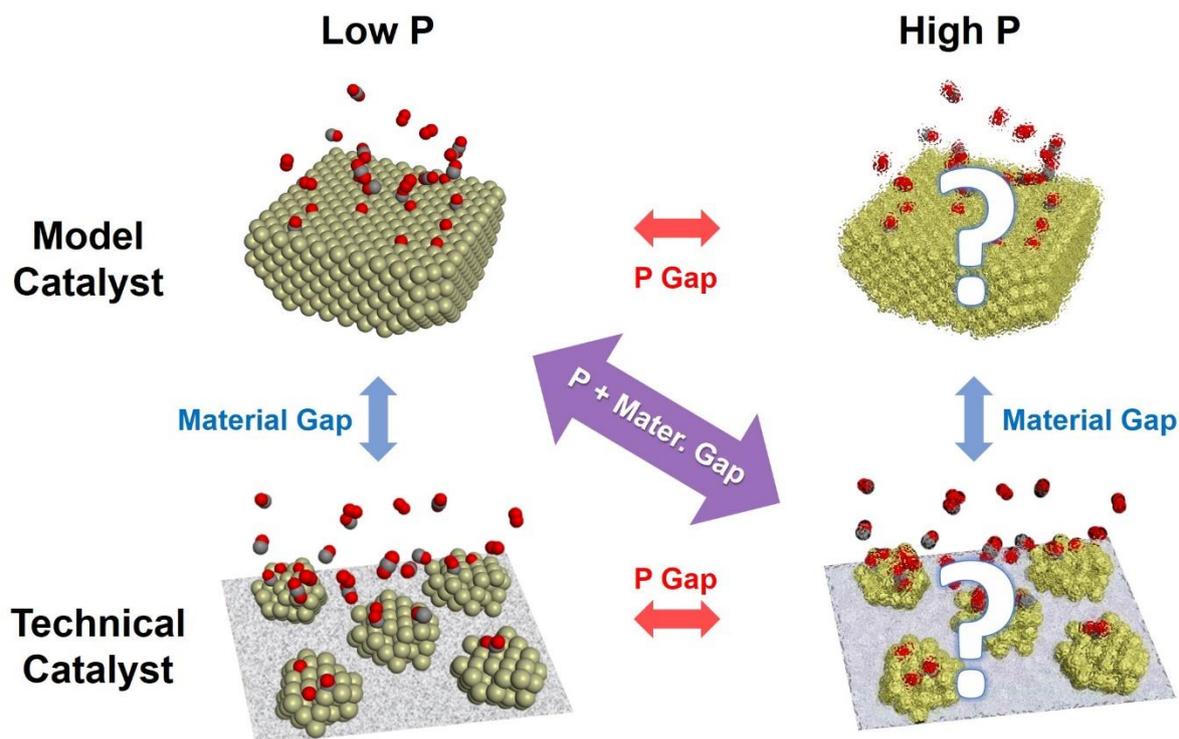


Fig. 1 **Pressure and material gaps in catalysis.** High reaction pressure can induce formation of meta-stable active structures often over and near the catalyst surface, which cannot be observed at low pressure conditions, causing the so-called pressure gap. The nanostructures of most technical catalysts can undergo more facile and drastic structural changes, resulting in enhanced formation of distinct catalytic active surfaces, causing the so-called material gap. When the two gaps are combined, the mechanistic differences in catalytic actions between model system and the system of industrial relevance are too large to be comparable. These combined large gaps have likely caused the reported discrepancies on the active structures of Cu-Zn catalysts in methanol synthesis as explained in the contribution of Beck et al. in *Nature Catalysis*<sup>8</sup>.