

Exsolution Catalysts—Increasing Metal Efficiency

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Exsolution catalysts are perovskite oxide-based materials that can exsolve catalytically active dopant elements as nanoparticles covering the surface, while the perovskite backbone can act as a stable support material. Thus, under proper conditions, a highly catalytically active and stable catalyst surface can be achieved. For many catalytic materials, precious metals or non-abundant elements play a key role in high catalytic activity. As these elements are often expensive or their supply is ecologically and ethically problematic, the replacement, or at the least reduction in the necessary amount used, is a common aim of current research. One strategy to do so is utilizing exsolution catalysts, as the active elements can be very selectively exsolved, and hence only very small doping amounts are sufficient for excellent results. This approach enables catalyst design with very high active metal efficiency.

heterogeneous catalysis

perovskites

exsolution

supported nanoparticles

doping

Heterogeneous catalysis is the backbone of our modern society. Many large scale industrial processes depend on catalysts, e.g., the production of fertilizers, fuels, solvents or base chemicals [\[1\]](#). Additionally, with the current demand for a sustainable future without dependence on fossil fuels, heterogeneous catalysis is becoming crucially important [\[2\]](#). The major focus is on either utilizing CO₂ (as an abundant carbon source) or to find ways to store excess renewable energy in a practical way (e.g., by chemical energy conversion) [\[3\]](#).

Although many catalytic processes have been established for years, a constant development of catalyst materials remains necessary to increase efficiency and economic profitability. This is the driving force for numerous studies for novel catalyst materials or the improvement of existing systems. A common goal of all the current research efforts is the desire to reduce the amount of used precious metals or non-abundant elements [\[4\]](#), and, in spite of that, keeping or even improving catalytic performance. The need for this arises because several raw metals sources are very rare or their supply is ecologically and ethically problematic. Furthermore, in situ (operando) spectroscopic or microscopic techniques for catalyst characterisation in reaction environments are now highly advanced, thus enabling novel fundamental insights into reaction pathways and correlations between catalyst composition, structure and reactivity [\[5\]](#). Combining all this has opened various routes to strongly reduce the amount of required precious metals or to gradually replace them completely by cheaper materials, utilizing abundant oxides or metals. As a result, a new level of catalyst design has been reached.

The most widely used material class in heterogeneous catalysis are metal oxides. They play an important role either as a support material due to their specific properties (high surface area, porosity, reducibility, thermal stability, etc. [\[6\]](#)) or as a catalytically active phase (especially for redox mechanisms [\[7\]](#)). For example, mixed oxides

of Mo, V, Te and Nb are highly efficient catalysts for the selective oxidation of lower alkanes [8]. Hydrogen production by a high temperature water–gas shift (WGS) is traditionally conducted on CrO₃–Fe₂O₃ catalysts [9]. Moreover, supported metal catalysts utilize the oxide as the structural backbone, for high dispersion and for the stable anchoring of metal particles (ensuring a high surface area and thermal stability of the particles), thus also potentially improving the reactivity by creating an active interface or for, e.g., spill-over mechanisms. Widmann and Behm demonstrated that for CO oxidation on Au/TiO₂ catalysts, the necessary active oxygen species is only formed at the boundary of the Au–oxide interface, enabling high reactivity [10].

There are many other options for catalyst design and to reduce the amount of active metal species, ranging from carbon supported nanoparticles, through metal organic frameworks and hybrid materials to single atom catalysis and others, which are discussed in detail in, e.g., the great book from Chorkendorff and Niemantsverdriet [11]. In this article, we want to highlight the possibility to reduce the amount of active metal species by utilizing the very versatile materials class of (doped) perovskite oxides [12].

Perovskite oxides have the general formula ABO₃ with A and B being large and small cations, respectively. In terms of catalysis, the most interesting feature of this materials class is that the B-site can be doped with catalytically active elements. Consequently, the perovskite host lattice acts as a reservoir that can release these dopants: either upon reductive treatment or in reducing reaction environments. During exsolution, dopants migrate to the surface where they form stable nanoparticles, thus creating highly active catalyst surfaces [13].

With our own research, we want to demonstrate how this exsolution approach can serve as an elegant pathway to reduce the amount of catalytically active elements necessary for an excellent catalyst. We show this in this work through the example of the reverse water–gas shift reaction (rWGS), conducted on a perovskite host lattice with Co-doping on the B-site and a stepwise reduction in the amount of active cobalt by varying the catalyst composition. Even using a low Co-doping yielded very promising results.

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