

Christian Hess

# Mechanistic Insight into CO<sub>2</sub> Activation Using New Operando and Transient Spectroscopic Approaches

## Motivation and methodology

The use of atmospheric or locally emitted carbon dioxide (CO<sub>2</sub>) as raw material for the production of chemicals and fuels represents an important strategy for reducing the CO<sub>2</sub> concentration in the atmosphere and the dependence on fossil fuels. Heterogeneously catalyzed processes enable the activation and transformation of CO<sub>2</sub>, for example, via CO<sub>2</sub> hydrogenation, via reforming of CO<sub>2</sub> or by using CO<sub>2</sub> as an oxidizing agent in selective oxidation reactions. The rational design of better catalysts requires a fundamental understanding of the underlying reaction mechanism and the catalyst's mode of operation. To this end, the development and application of new experimental approaches is urgently needed, providing a detailed analysis of the respective catalyst and its structural dynamics, ultimately enabling the identification of reaction intermediates and active sites. To be of relevance, catalysts need to be monitored in situ under real working conditions, preferably combined with a simultaneous detection of activity, which is known as operando analysis (see Fig. 1).

Typically, catalyst surfaces are dominated by silent spectator species, which do not participate in the reaction, while the active species are hidden. It is therefore highly desirable to allow for a discrimination between active species and spectator species, thereby increasing the sensitivity for the active species. This can be achieved by the use of transient spectroscopic approaches, for example, modulation-excitation spectroscopy (MES) [1]. In such experiments, typically a modulation of the concentration is applied by periodically switching the gas. The modulation is then translated into the active (i.e. actively responding) species and hence the overall signal, while the spectator species and the noise do not follow the modulation and can be removed by frequency filtering, referred to as phase-sensitive detection (PSD). As a result, the species actively participating in the reaction as well as the sequence in which they appear can be identified, providing detailed information on reaction mechanisms and key species, that is, catalytically active species and active sites.

## Examples from current research

In the following, the potential of operando and transient spectroscopic approaches for mechanistic insight into heterogeneously catalyzed reactions will be illustrated for CO<sub>2</sub> activation over reducible oxide catalysts. As first example, the hydrogenation of CO<sub>2</sub> to CO and H<sub>2</sub>O, i.e., the reverse water-gas shift reaction (rWGS), over ceria-supported gold catalysts will be discussed [2]. For the rWGS over oxide-supported catalysts mainly two general types of reaction mechanisms have been proposed in the literature, that is, redox and associative mechanisms. While the redox mechanism consists of a reaction of lattice oxygen with hydrogen, leading to water and oxygen vacancy formation, which is followed by reoxidation of the catalyst by CO<sub>2</sub>, in associative mechanisms carbon- and oxygen containing intermediates (e.g. carbonates, formates, carboxyls) are formed. The critical assessment of reaction mechanisms has been a major challenge, but as will be demonstrated below, can now be addressed in a targeted manner by the combined use of operando and transient spectroscopic methods [3].

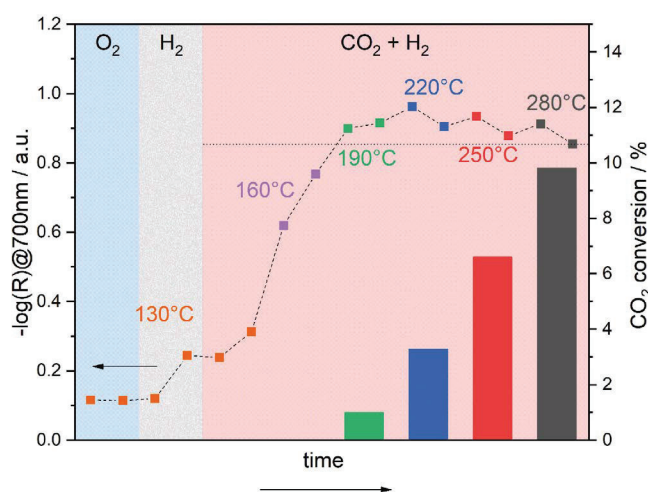
Supported catalysts are commonly distinguished based on the nature of the used support material, which can be either inactive (e.g. SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>) or active (e.g. TiO<sub>2</sub>, CeO<sub>2</sub>). The latter supports have been proposed to enhance the catalytic activity based on their active participation in the reaction mechanism. Over the years, we have systematically explored the use and (facet-dependent) mechanistic behavior of ceria (CeO<sub>2</sub>), which is among the catalytically most active metal oxides and exhibits particular redox properties and a relatively high abundance [4]. Here, we will highlight its role as an active support in low-loaded gold catalysts, which are characterized by the presence of highly dispersed gold, by using different ceria support materials (polyhedra, polycrystalline sheets). While the combination of operando Raman and UV-Vis spectra during rWGS reveals that the oxygen vacancy concentration is not rate-determining, transient IR spectroscopy including MES confirms the dominance of an associative mechanism and provides detailed information on CO<sub>2</sub> reduction via formation of carbonates (and formates) and H<sub>2</sub> activation via its dissociation on gold [2].

Reactivity experiments on indium oxide have revealed that the presence of a noble metal is not essential for CO<sub>2</sub> activation. As second example, we address the rWGS over cubic In<sub>2</sub>O<sub>3</sub> nanoparticles from a mechanistic point of view [5]. In situ/operando monitoring of the absorbance at 700 nm, which is used as an

Prof. Dr. Christian Hess  
Institut für Physikalische Chemie  
Technische Universität Darmstadt  
Peter-Grünberg-Str. 8, D-64287 Darmstadt  
christian.hess@tu-darmstadt.de  
<https://www.chemie.tu-darmstadt.de/hess/index.en.jsp>

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indicator for oxygen defects, highlight the relevance of redox processes in  $\text{In}_2\text{O}_3$  (see Fig. 1). Systematic investigation of the related reduction and oxidation processes and their comparison to reaction conditions reveals that reduced surface indium oxide can be re-oxidized by  $\text{CO}_2$ , while complete oxidation of the bulk is only possible with  $\text{O}_2$  [6]. To gain insight into charge and mass transport, operando impedance spectra show a pronounced contribution of the inductive part, which is attributed to the percolation of  $\text{In}_2\text{O}_3$  nanoparticles with hydrogen species [5]. In contrast to exposure to  $\text{H}_2$ , under reaction conditions  $\text{In}_2\text{O}_3$  is strongly but not fully reduced. These findings highlight the importance of oxygen/hydrogen dynamics during  $\text{CO}_2$  hydrogenation over  $\text{In}_2\text{O}_3$  catalysts, besides surface processes, which are currently being explored.



**Fig. 1:** In situ/operando UV-Vis spectroscopic results (at 700 nm) for cubic  $\text{In}_2\text{O}_3$  nanoparticles, recorded during  $\text{O}_2$  and  $\text{H}_2$  exposure at 130 °C and reaction conditions ( $\text{CO}_2:\text{H}_2$ , 2:4) ranging from 130 to 280 °C in 30 °C steps. From 190 °C on,  $\text{CO}_2$  is activated towards rWGSr, and the conversions are shown by bars (right axis). The exposure time before the conditions were changed was ca. 30 min. The horizontal dotted line helps to illustrate the change in absorbance under reaction conditions [5].

As third example, the oxidative dehydrogenation (ODH) of propane is addressed, which is an exothermic process not subject to thermodynamic limitations or coking, in contrast to dehydrogenation. Supported vanadium oxides are among the most active ODH catalysts but their detailed mode of operation, including the active vanadium sites and adsorbate dynamics, has only recently been unraveled by applying a combination of operando spectroscopies (UV-Vis, Raman, IR) and, in particular, (isotopic) IR-MES coupled with PSD [7]. The use of  $\text{CO}_2$  as soft oxidant may suppress overoxidation, which is the major challenge in propane ODH, and shift the equilibrium to the product side. To provide insight into the complex reaction network, operando resonance Raman spectroscopy was applied, which reveals distinct changes in the surface vanadia and support structure [8]. While the mechanistic work is ongoing, our current results are consistent with the occurrence of two parallel reaction pathways, that is, direct ODH to propene and CO and dehydrogenation followed by rWGSr.

## Conclusions


Our findings highlight the potential of recently developed combined operando/transient spectroscopic approaches for

obtaining mechanistic insight into heterogeneously catalyzed  $\text{CO}_2$  activation and transformation processes, such as  $\text{CO}_2$  hydrogenation or  $\text{CO}_2$ -assisted dehydrogenation. The use of modulation excitation spectroscopy coupled with phase-sensitive detection is expected to gain more importance in future mechanistic studies due to its capabilities to discriminate between active and spectator species and to identify catalytically active species and sites.

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## Prof. Dr. Christian Hess



Christian Hess studied chemistry at the universities of Würzburg, Cambridge/UK, and Göttingen, and obtained his PhD at the Fritz Haber Institute in Berlin. After post-doctoral research at Texas A&M University and UC Berkeley/Lawrence Berkeley National Laboratory (LBNL) as a Feodor-Lynen and Otto-Hahn Fellow, he returned to the Fritz Haber Institute to lead an Emmy Noether Group. Since 2008 he has been professor in physical chemistry at TU Darmstadt. In 2015 he was visiting professor at Haldor Topsoe/DK. His scientific interests are focused on a detailed understanding of structure-activity relationships of functional materials using in situ/operando/transient spectroscopy. His research group works on heterogeneous catalysis and gas sensing, including chemical energy storage, selective oxidation, surface functionalization,  $\text{NO}_x$  abatement, metal-oxide gas sensors, and the development and application of in situ/operando/transient approaches with a focus on vibrational spectroscopy.