Elucidating the CO_2 Activation in the Context of the Reverse Water Gas Shift Reaction

Project Manager
Marc Ziemba

Researchers
Dr. M. Verónica Ganduglia-Pirovano

Principal Investigator
Prof. Dr. Christian Hess

Project Term
2020 - 2021

Clusters
Lichtenberg Cluster Darmstadt

Software
VASP

Institute
Eduard-Zintl-Institut

University
Technische Universität Darmstadt

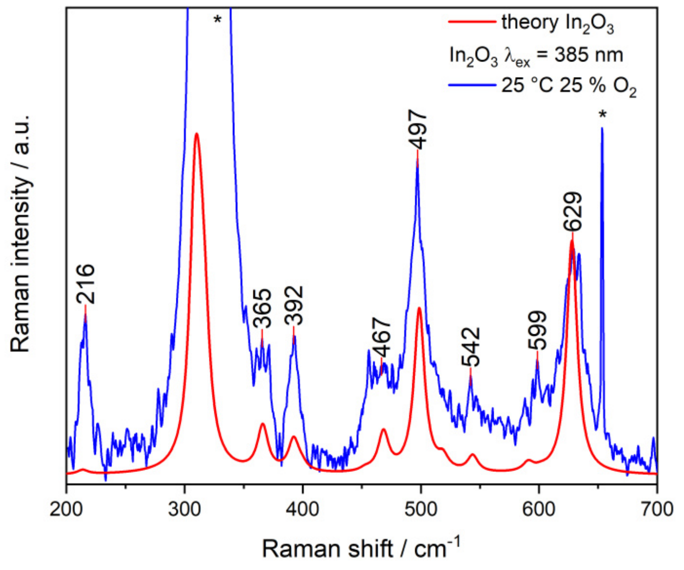

Figure 1: Comparision of a theoretical (DFT) Raman spectrum of a non-defective primitive In_2O_3 cell (red) and an in situ 385 nm Raman spectrum (blue) of In_2O_3 recorded at 25 °C in 25% O_2/H_2. The asterisks (*) mark bands originating from the CaF_2 window, while the sharp feature at around 650 cm^{-1} results from cosmic rays.

Introduction

The aim of the last project was to understand the CO_2 activation over Au and Cu loaded ceria and bare indium oxide. In the framework of the reverse water-gas shift reaction (rWGSR), which is of interest for the production of syn gas, we have investigated this reaction experimentally. However, it is important to understand the interactions of the reactants with the support or metal in more detail to be able to identify possible reaction intermediates. Therefore, a combination of density functional theory (DFT), Raman spectroscopy and DRIFTS will be used to allow for interpretations at the molecular level. Within this combination of theory and experiment it is possible to gain new insight into reaction mechanisms and the influence of the metal, the support as well as the metal support interactions.

Methods

The general procedure is to perform a structure relaxation with tight convergence criteria within the PBE framework. Then, a vibrational analysis is performed, which involves the calculation of normal modes employing a method based on density functional perturbation theory (DFPT), followed by the calculation of IR and/or Raman activities. The calculation of Raman intensities is computationally demanding due to the fact that it depends on the third order derivative of the energy. These calculations, i.e., the simulations of the Raman and IR spectra, run in close interaction with the corresponding experiments to provide a direct interpretation of the experimental results.

Results

In this project, the aim was to better understand our experimental findings during the rWGSR over Au/CeO_2(111) catalysts. In this context, we would like to briefly discuss the interaction of H_2 with gold deposited on CeO_2(111). Transient DRIFTS measurements were able to detect bands that could be assigned to specific hydrogen species adsorbed on Au_x/CeO_2(111) using DFT. More precisely, we could follow the H_2 dissociation over Au/CeO_2, since both species (H_2-Au and H-Au) have characteristic bands. The latter H-Au vibration has previously been proposed to be associated with a band at 2134 cm^{-1}. This assignment could be confirmed theoretically by our calculations. The H_2-Au band (1943 cm^{-1}) has not been observed before. In summary, it can be said that our calculations allowed a better interpretation of different vibrational bands and thus a better mechanistic understanding of overall reaction. Another part addressed the interpretation of Raman spectra of cubic In_2O_3 and its defect chemistry. In this context, we calculated Raman spectra of clean as well as defect-rich In_2O_3 and were able to unambiguously assign the nature as well as its symmetry of defect-associated bands for the first time. This opens an important basis for a better interpretation of In_2O_3 spectra in catalytically relevant processes. Finally, the interactions of H_2 or CO with In_2O_3(111) could be investigated in more detail, which will be linked to experimental results in the near future.

Discussion

It should be mentioned that the calculations are/were done within the PBE+U or PBE framework, which is a reasonable approximation in terms of vibrational modes. This is, however, different for electronic structures, for which the use of hybrid functionals (HSE06) is essential, which should also be a topic in the future. Furthermore, mainly bulk properties of In_2O_3 were calculated as the first step, but for catalytic processes the properties of the surface are of more relevance. Therefore, in the future mainly two surface terminations of In_2O_3 will be considered in more detail, the 111 and the 110 termination. Furthermore, previous studies have shown that metallic indium occurs under reaction conditions, so its influence will also be considered in more detail. Due to the symmetry-induced size of the systems, these systems are computationally quite elaborate, hence the use of a high performance computer is essential.

Publications

Schilling, C.; Ziemba, M.; Ganduglia-Pirovano, M. V.; Hess, C.: Identification of Single-Atom Active Sites in CO Oxidation Over Oxide-Supported Au Catalysts. J. Catal., 2020, 383, 264–272. https://doi.org/10.1016/j.jcat.2020.01.022

Ziemba, M.; Ganduglia-Pirovano, M. V.; Hess, C.: Elucidating the Oxygen Storage-Release Dynamics in Ceria Nanorods by Combined Multi-Wavelength Raman Spectroscopy and DFT. J. Phys. Chem. Lett. 2020, 8554–8559. https://doi.org/10.1021/acs.jpclett.0c02607

Ziemba, M.; Hess, C.: Influence of Gold on the Reactivity Behaviour of Ceria Nanorods in CO Oxidation: Combining Operando Spectroscopies and DFT Calculations. Catal. Sci. Technol. 2020, 10 (11), 3720–3730. https://doi.org/10.1039/D0CY00392A

Ziemba, M.; Stark, D.; Hess, C.: Combined DFT and Operando Spectroscopic Study of the Water-Gas Shift Reaction over Ceria-Based Catalysts : The Role of the Noble Metal and Ceria. Chem. Proc. 2020, 2 (111), 1–5. https://doi.org/10.3390/ECCS2020-07531

Ziemba, M.; Schilling, C.; Ganduglia-Pirovano, M. V.; Hess, C.: Toward an Atomic-Level Understanding of Ceria-Based Catalysts: When Experiment and Theory Go Hand in Hand. Acc. Chem. Res. 2021, 54 (13), 2884–2893. https://doi.org/10.1021/acs.accounts.1c00226

Ziemba, M.; Schumacher, L.; Hess, C.: Reduction Behavior of Cubic In2O3 Nanoparticles by Combined Multiple In Situ Spectroscopy and DFT. J. Phys. Chem. Lett. 2021, 12 (15), 3749–3754. https://doi.org/10.1021/acs.jpclett.1c00892

Ziemba, M.; Weyel, J.; Hess, C.: Elucidating the Mechanism of the Reverse Water–Gas Shift Reaction over Au/CeO2 Catalysts Using Operando and Transient Spectroscopies. Appl. Catal. B Environ. 2022, 301 (October 2021), 120825. https://doi.org/10.1016/j.apcatb.2021.120825

Reference

Schilling, C.; Hofmann, A.; Hess, C.; Ganduglia-Pirovano, M. V.: Raman Spectra of Polycrystalline CeO2: A Density Functional Theory Study, J. Phys. Chem. C, 2017, 121(38), 20834–20849. https://doi.org/10.1021/acs.jpcc.7b06643

Schilling, C.; Ganduglia-Pirovano, M. V.; Hess, C.: Experimental and Theoretical Study on the Nature of Adsorbed Oxygen Species on Shaped Ceria Nanoparticles, J. Phys. Chem. Lett., 2018, 9, 6593-6598. https://doi.org/10.1021/acs.jpclett.8b02728

Schilling, C.; Hess, C.: Real-Time Observation of the Defect Dynamics in Working Au/CeO2 Catalysts by Combined Operando Raman/UV-Vis Spectroscopy. J. Phys. Chem. C, 2018, 122(5), 2909–2917. https://doi.org/10.1021/acs.jpcc.8b00027

Schilling, C.; Hess, C.: Elucidating the Role of Support Oxygen in the Water–Gas Shift Reaction over Ceria-Supported Gold Catalysts Using Operando Spectroscopy. ACS Catal., 2019, 9, 1159–1171. https://doi.org/10.1021/acscatal.8b04536

Ziemba, M.; Ganduglia-Pirovano, M. V.; Hess, C.: Insight into the Mechanism of the Water-Gas Shift Reaction over Au/CeO2 Catalysts Using Combined Operando Spectroscopies. Faraday Discuss. 2020. https://doi.org/10.1039/C9FD00133F

Last Update: 2022-11-02 15:51