Combined DFT and *operando* spectroscopic study of the water-gas shift reaction over ceria-based catalysts: the role of the noble metal and ceria faceting

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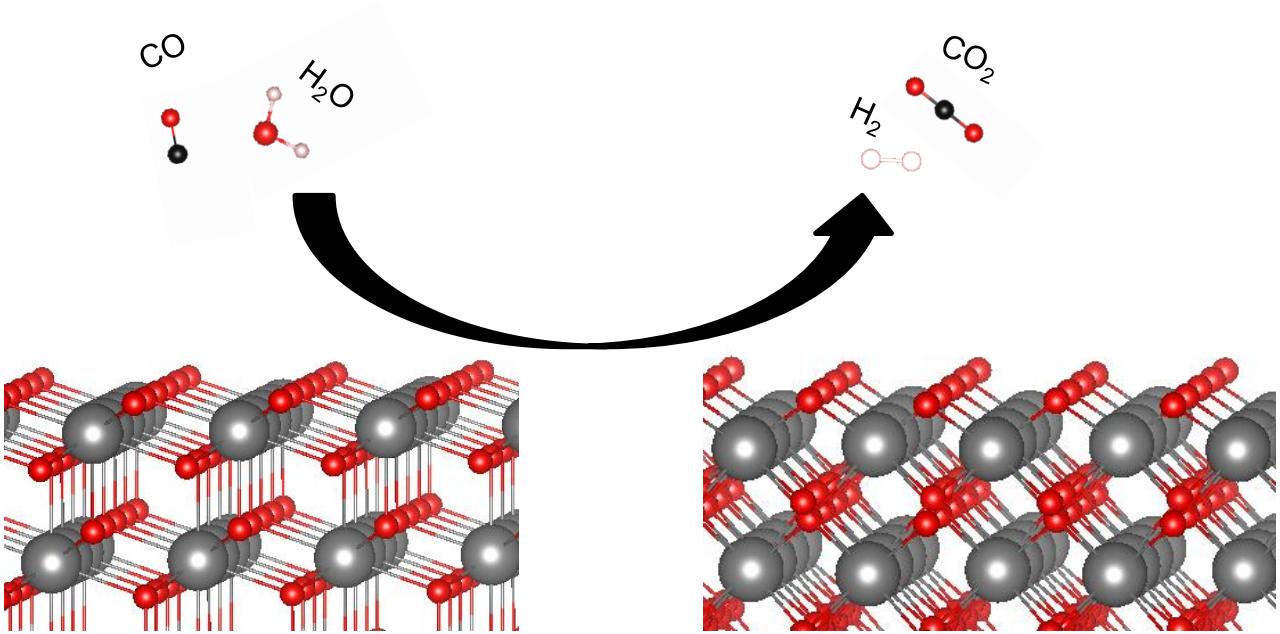
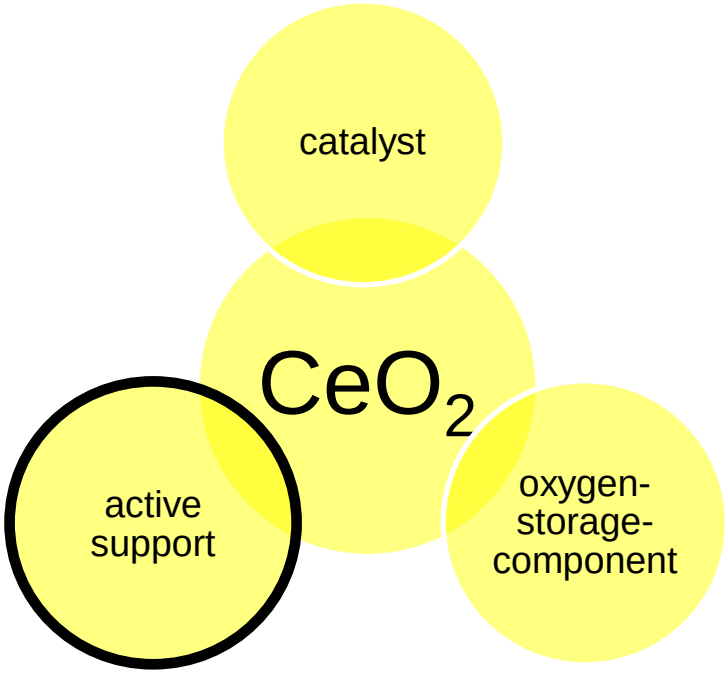
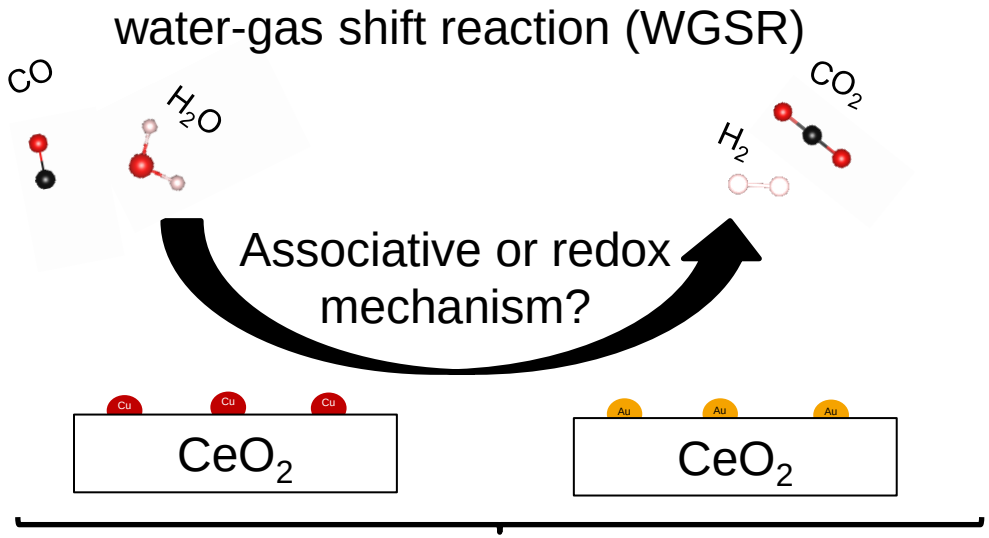


$CeO_2(111)$ $CeO_2(100)$

Background and motivation



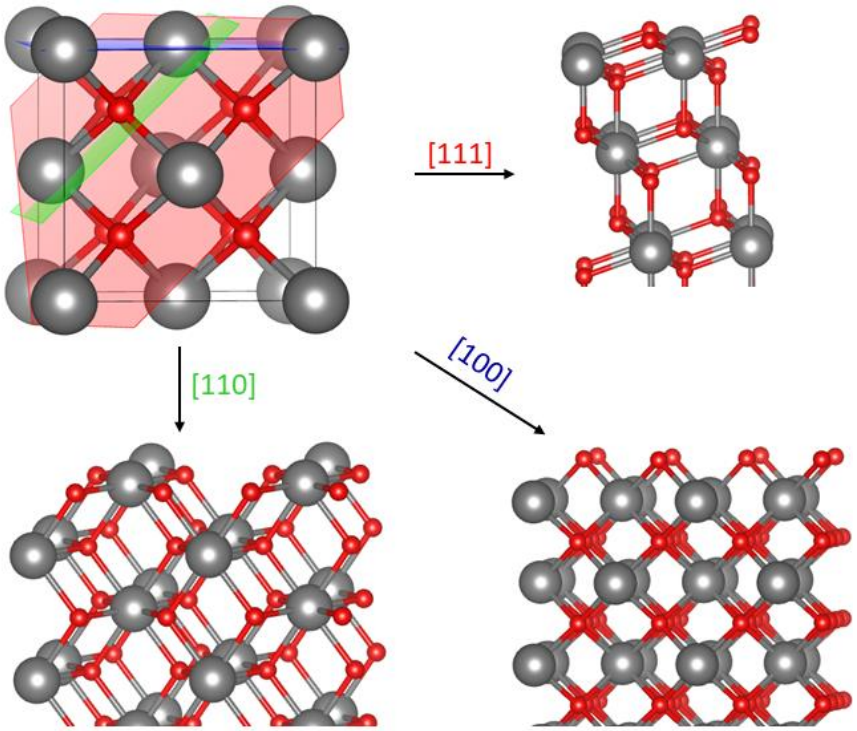


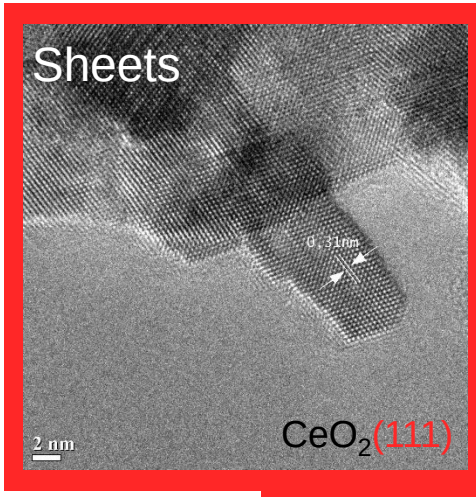
Which aspects are of importance for this reaction?

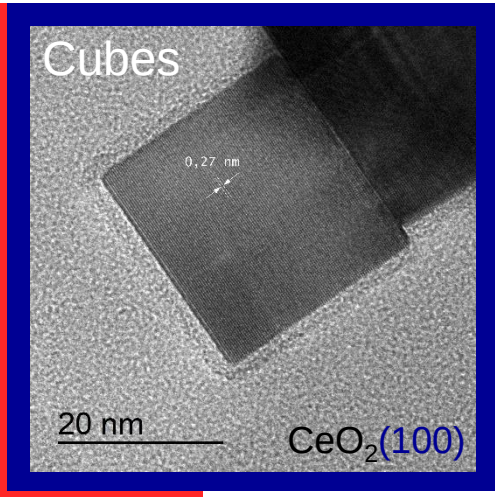
- defect formation energy
- redox properties of Ce
- water dissociation
- metal-support interaction

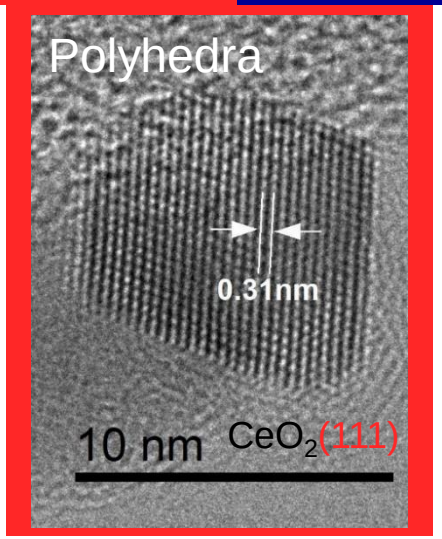
These properties depend on the cerium oxide surface facet and the type of metal!

Ceria surface facets









In collaboration with Prof. H.-J. Kleebe (TU Darmstadt)

Experimental and theoretical approach

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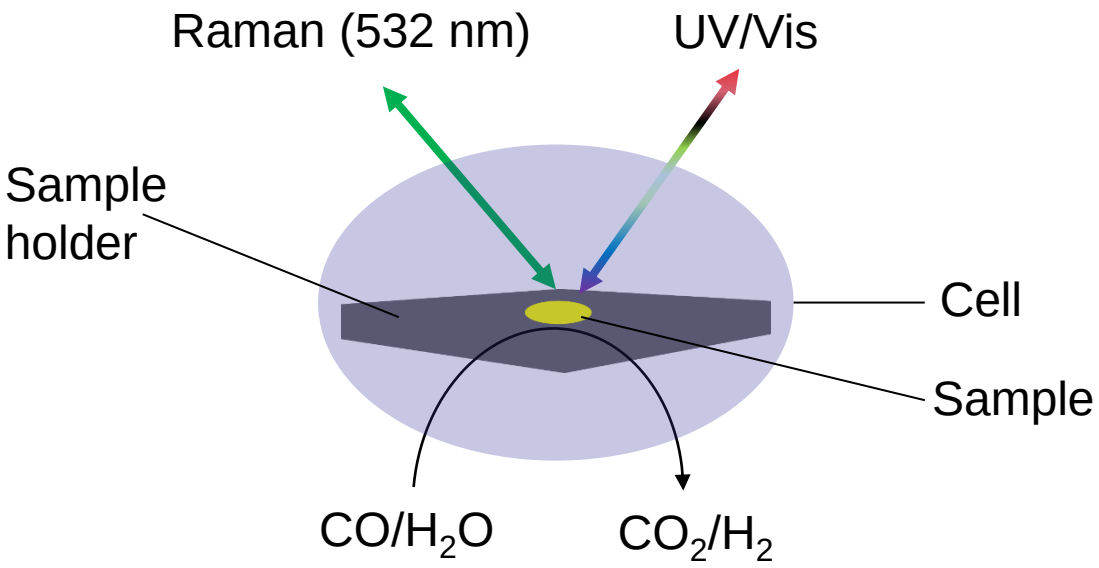
Operando spectroscopy



Density Functional Theory

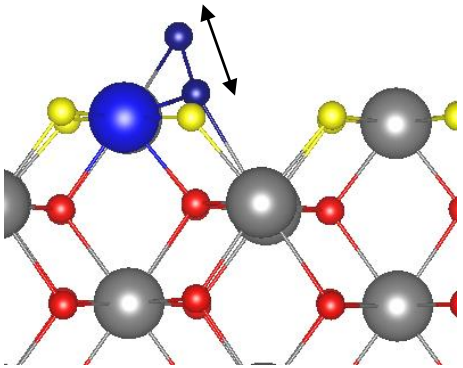
PBE+U / 4.5 eV

↓

DFPT

↓

Raman spectra



Schilling, C.; Hofmann, A.; Hess, C.; Ganduglia-Pirovano, M.V. *J. Phys. Chem. C* **2017**, *121*, 20834–20849, doi:10.1021/acs.jpcc.7b06643.

Experimental details

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Synthesis of the ceria samples

Sheets: thermal decomposition[1]

Cubes: hydrothermal synthesis[2]

Polyhedra: commercial sample

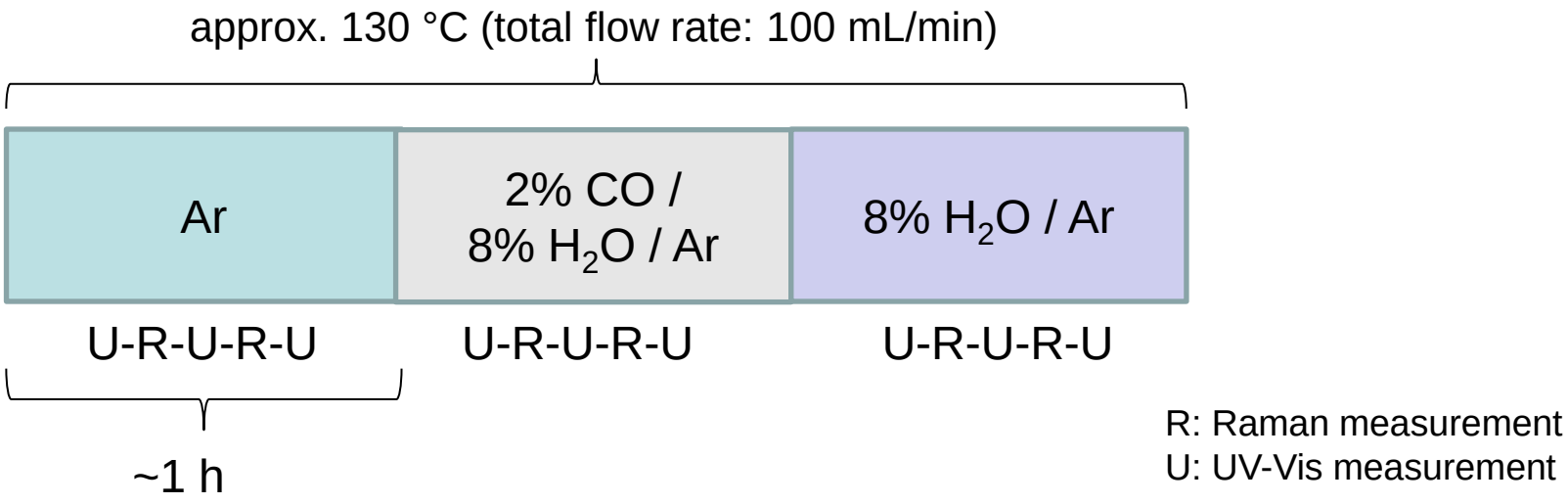
(Sigma Aldrich, <25 nm (BET))

Metal loading (target: 0.5 wt% metal)

Gold loading: electrolyte deposition using $HAuCl_4 \cdot 8H_2O$[1]

Copper loading: incipient wetness impregnation using $Cu(NO_3)_2 \cdot 3H_2O$ and 500 °C

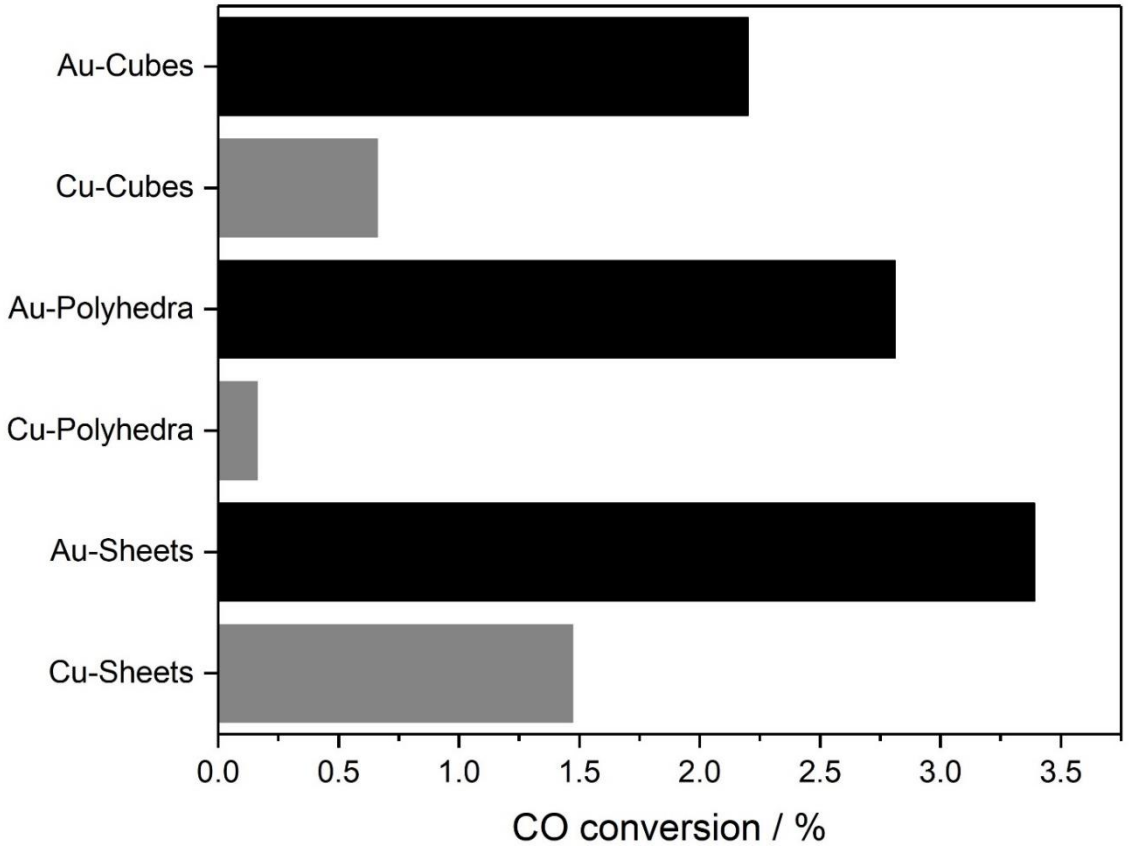
Loading confirmed by ICP-OES



R: Raman measurement
U: UV-Vis measurement

[1] Schilling, C. and Hess, C. *ACS Catal.* **2019**, *9*, 1159–1171, doi:10.1021/acscatal.8b04536.
[2] Ziemba, M. and Hess, C. *Catal. Sci. Technol.* **2020**, *10*, 3720–3730, doi:10.1039/D0CY00392A.

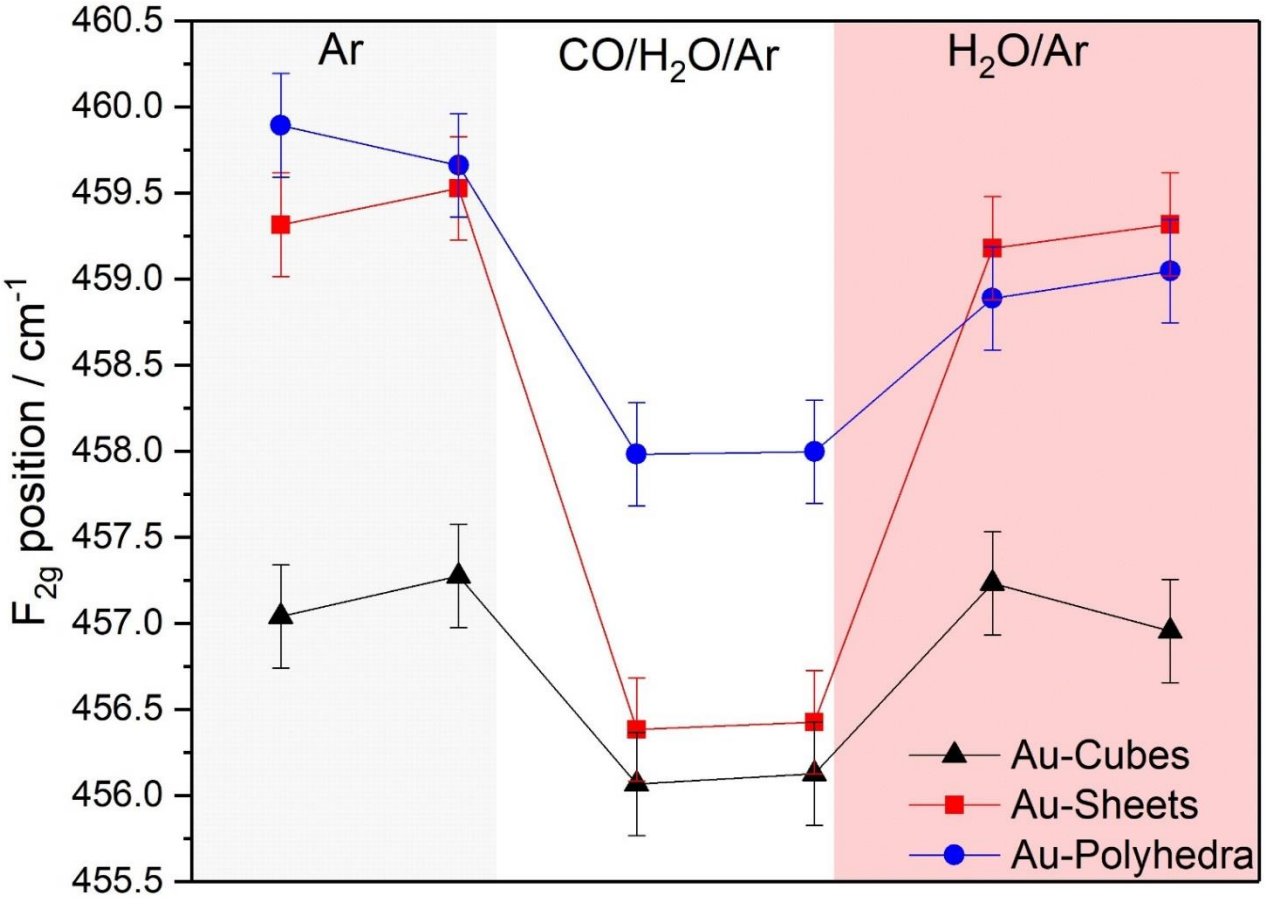
CO conversion over Au and Cu loaded ceria



WGSR activity of gold loaded catalysts is higher than for copper loaded ones.

CO conversion measured after at least 1h on stream at about 130 °C under 2 % CO and 8 % H_2O balanced in Ar (total flow: 100 mL/min).

Operando Raman spectroscopy @ Au/CeO_2



- F_{2g} shift is measure for near-surface oxygen defects.[3]
- F_{2g} red-shift from Ar to reaction conditions correlates with catalytic activity.
- Switching from reaction conditions to 8 % water leads to support oxidation (→ F_{2g} blue-shift).

[3] Schilling, C.; Hofmann, A.; Hess, C.; Ganduglia-Pirovano, M.V. *J. Phys. Chem. C* **2017**, *121*, 20834–20849, doi:10.1021/acs.jpcc.7b06643.

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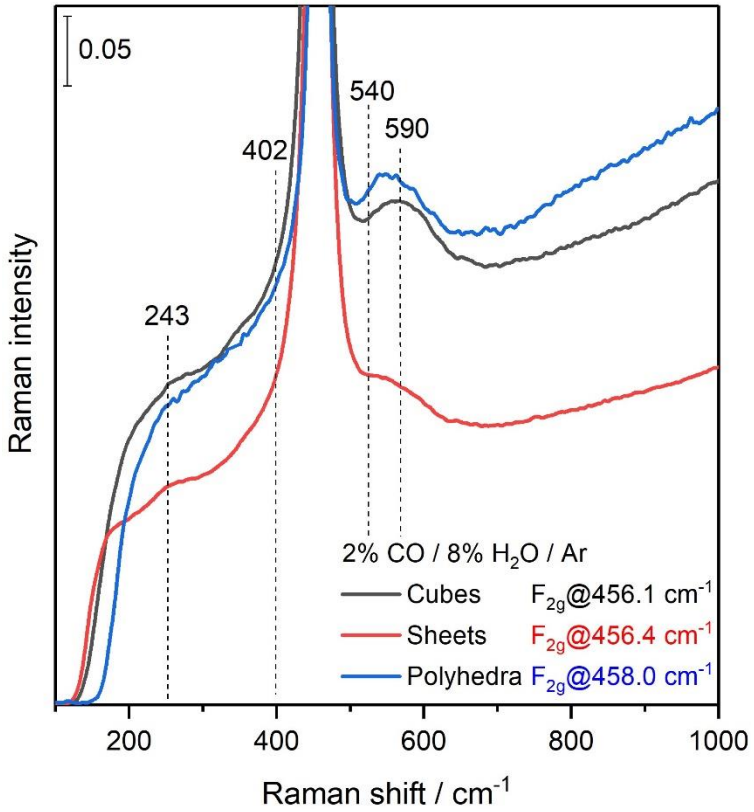
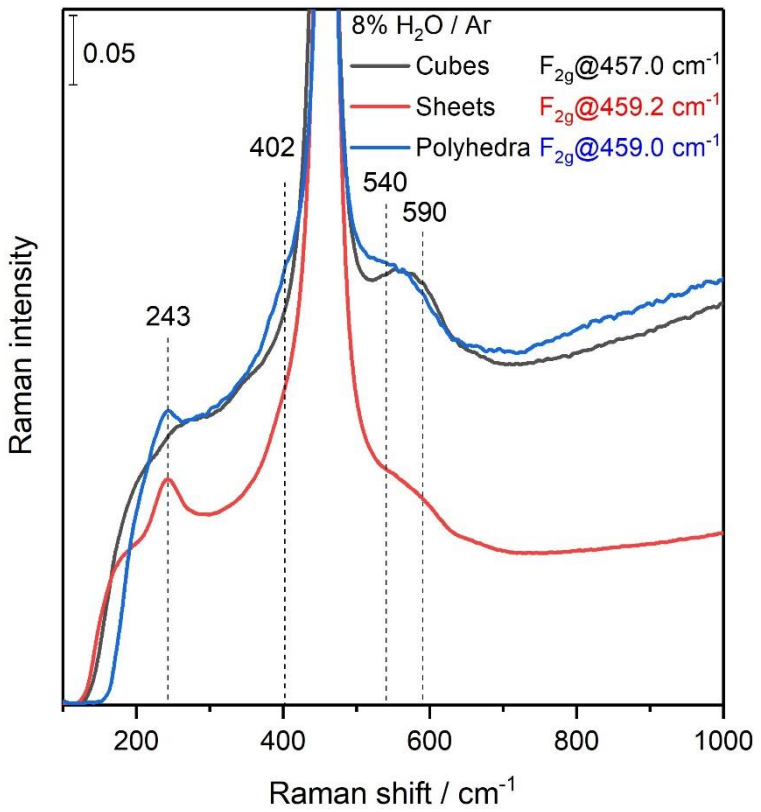
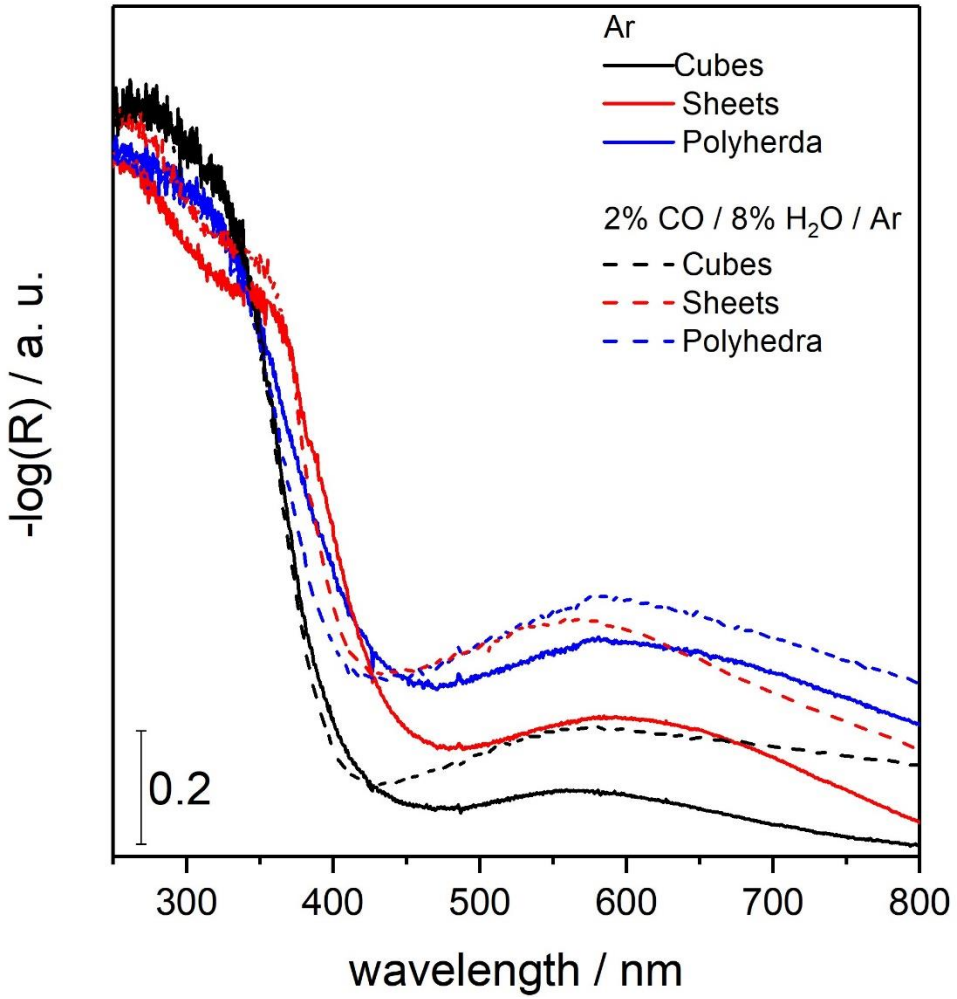




Longitudinal (243 cm^{-1}) and transversal (402 cm^{-1}) surface modes of CeO_2(111) disappear under WGSR conditions and reappear after switching to 8 % H_2O for sheets and polyhedra.

Operando UV-Vis spectroscopy @ Au/CeO_2



- Absorption above 450 nm increases during reaction conditions
  - Sheets show the greatest increase in absorption followed by cubes and polyhedra
- Absorption above 450 nm: $Ce^{3+} \rightarrow Ce^{4+}$ charge transfer transitions[4] (indicator for surface reduction)

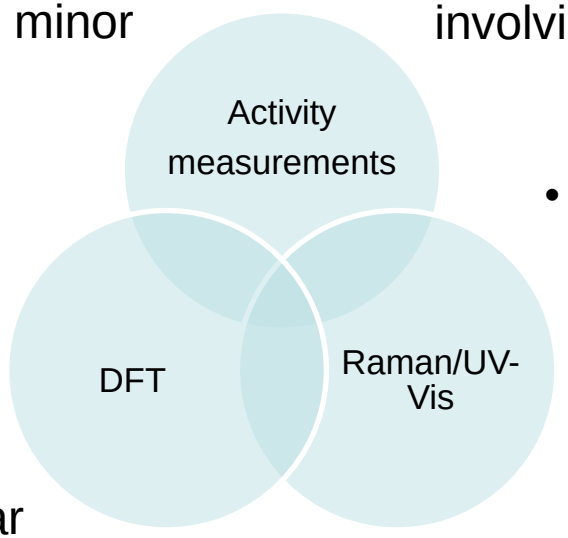
➢ Thus, the results are consistent with the results of the Raman measurements.

[4] Schilling, C. and Hess, C.. *J. Phys. Chem. C* **2018**, *122*, 2909–2917, doi:10.1021/acs.jpcc.8b00027.

Conclusions

The combination of *operando* spectroscopy and DFT calculations ….

- … shows that defect formation energy of ceria plays minor role for LT-WGSR.
- … confirms redox mechanism involving ceria lattice oxygen.
- … shows potential of stepped Au/CeO_2(111) catalysts.
- … demonstrates that water dissociates over reduced ceria and heals oxygen vacancies.
- … facilitates molecular understanding of LT-WGSR mechanism on ceria-based catalysts.
- … demonstrates importance of surface termination and facet-dependent metal-support interaction.



Acknowledgements

Hess working group

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Dr. Stefan Lauterbach

(TU Darmstadt)

TEM

Dr. Martin Brodrecht

(TU Darmstadt)

BET

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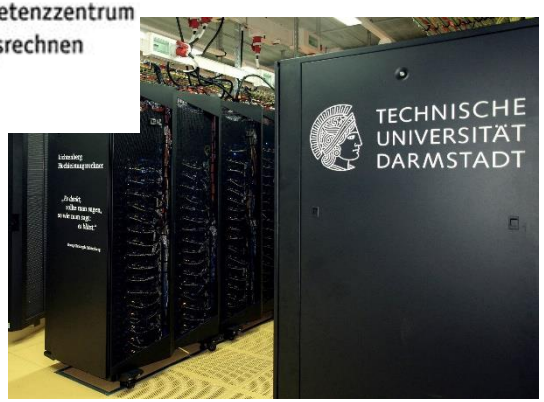
Dr. M. Verónica Ganduglia Pirovano

DFT

Hessisches Kompetenzzentrum für Hochleistungsrechnen



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Thanks for your interest in our work.

I am looking forward to your comments.