Karlsruhe Institute of Technology

Surface Faceting and Reconstruction of Ceria Nanoparticles

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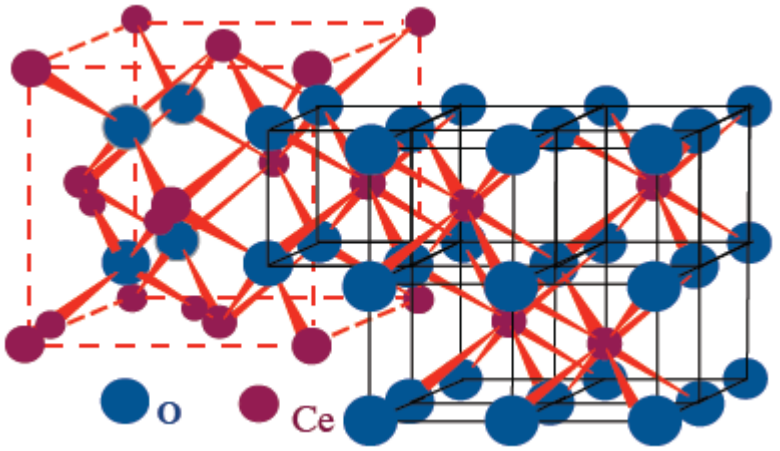
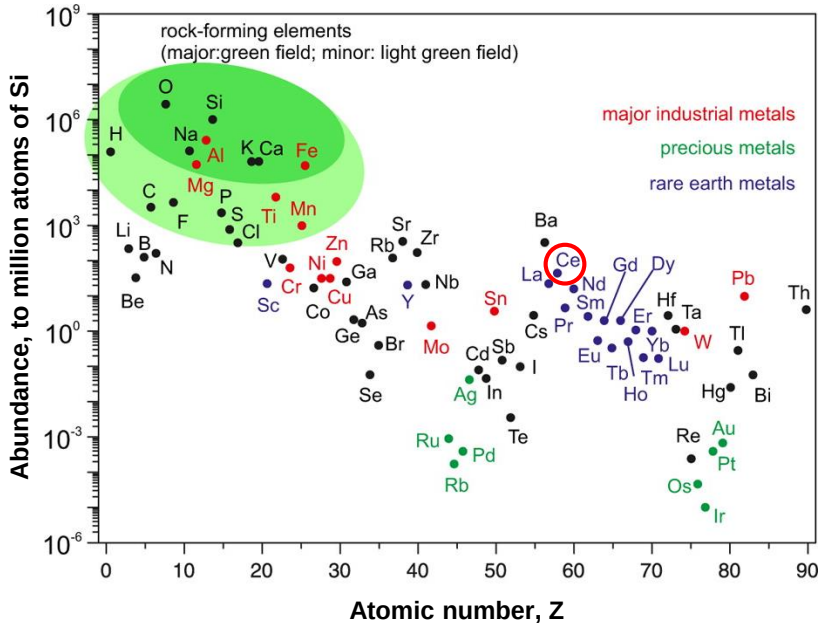
Institute of Functional Interfaces (IFG)

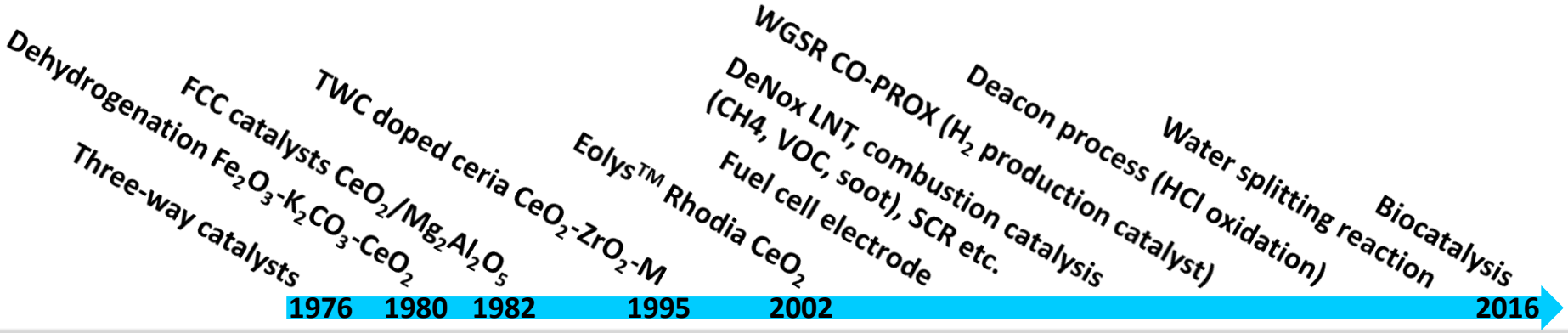


Why is ceria (CeO_2, cerium dioxide) interesting?



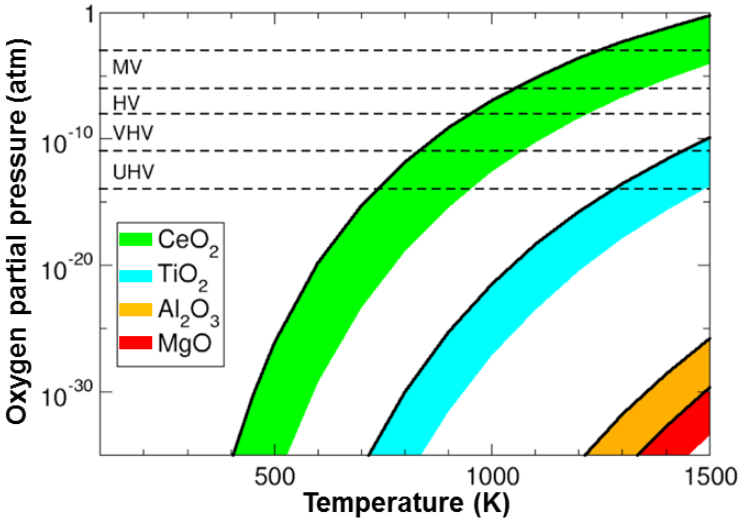
- **Reversible storage/release of oxygen atoms – oxygen storage capacity (OSC).**
- **Interconversion between $4f^1$-Ce(III) and $4f^0$-Ce(IV) oxidation states.**
- **Defects can be created by oxygen release and electron transfer.**
- **Promote electron and oxygen transfer.**
- **Promote dispersion of noble metals and thermal stability of the support.**

40 years of catalysis by ceria

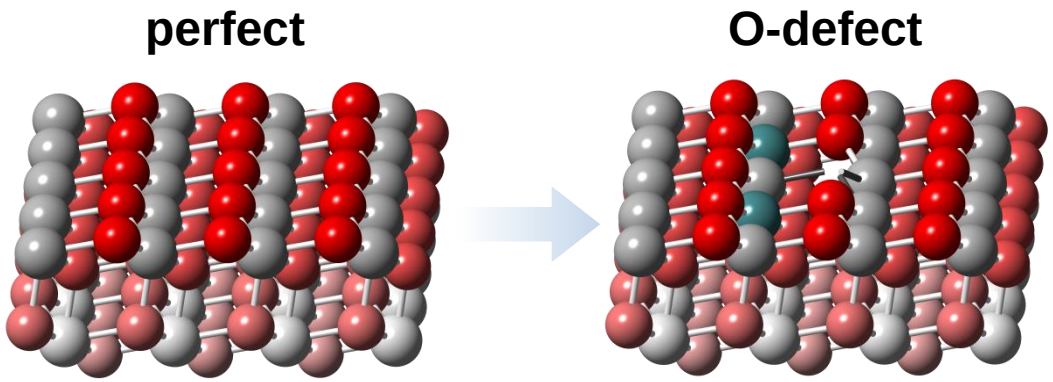


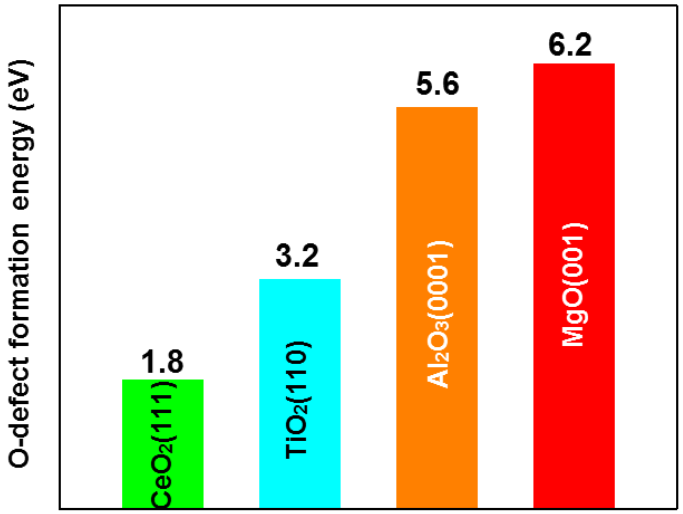
T. Montini, M. Melchionna, M. Monai, P. Fornasiero, *Chem. Rev.*, 2016, 116, 5987.
H. S. Gandhi, A. G. Piken, M. Schelef, R. G. Delosh, *SAE Tech. Papers*, 1976, 55, 760201.

Ceria has low oxygen vacancy formation energy



p(O_2) vs T phase diagram.





Calculated oxygen defect formation energy.

Stability and reducibility of ceria surfaces

Surface	Surface energy (J·m^{-2})	O-vacancy formation energy (eV)
(111)	0.68	2.60
(110)	1.01	1.99
(100)	1.41	2.27

M. Nolan et al., *Surf. Sci.*, 2005, 576, 217.
M. Nolan et al., *Surf. Sci.*, 2005, 595, 223.

J. Paier, C. Penschke, J. Sauer, *Chem. Rev.*, 2013, 113, 3949.

From single crystals to commercial powders

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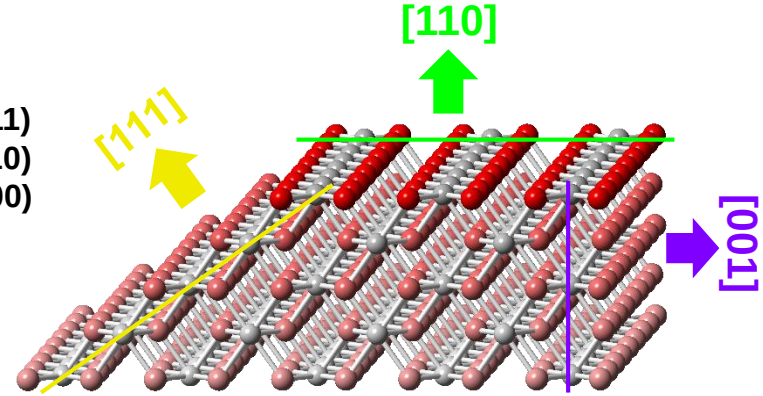
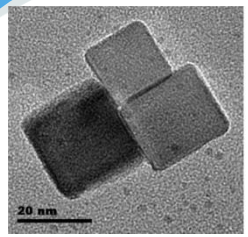
SXs

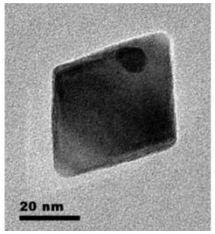
(111)
(110)
(100)



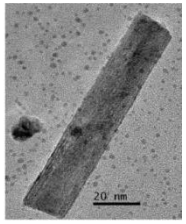
nano crystals



(100)

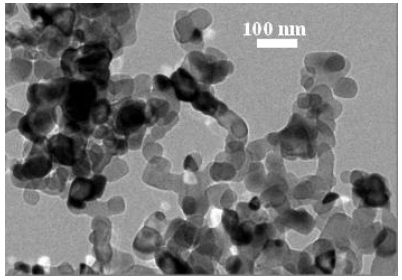


(111)

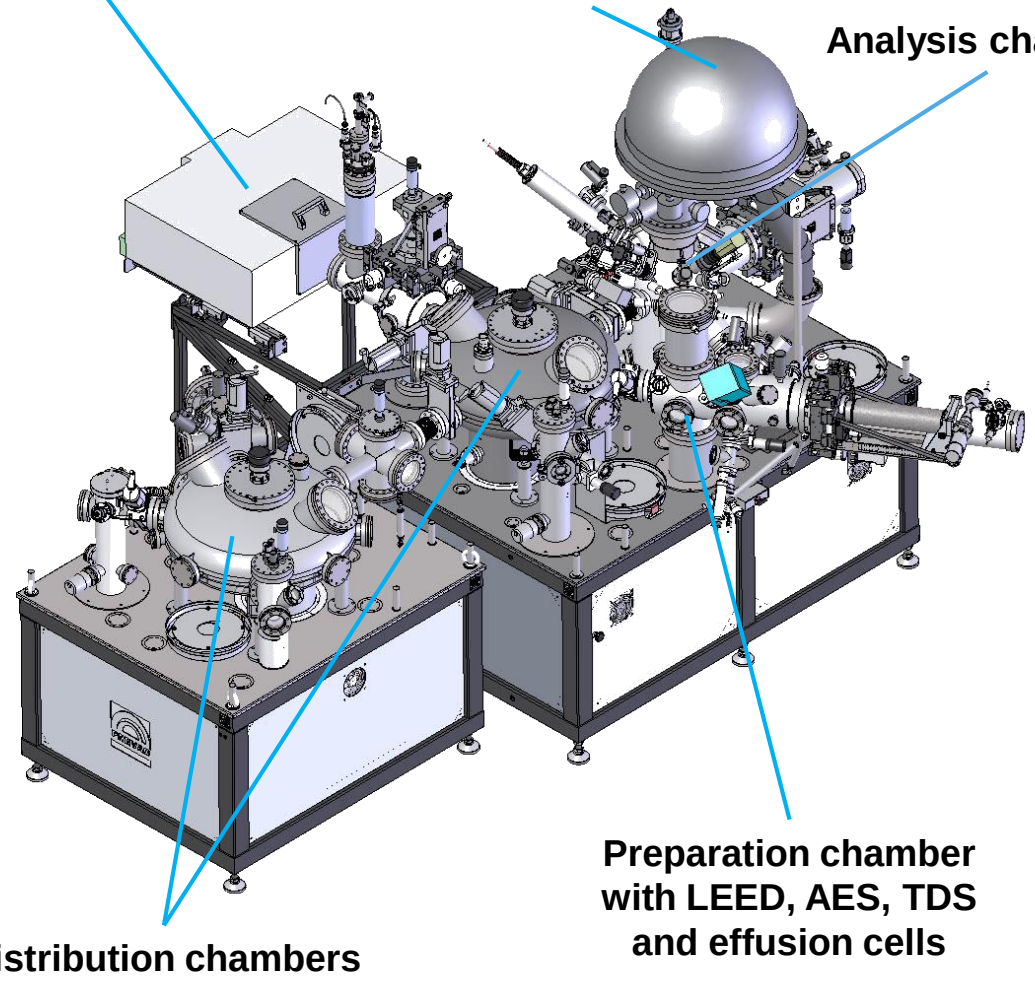


(110) + (100)

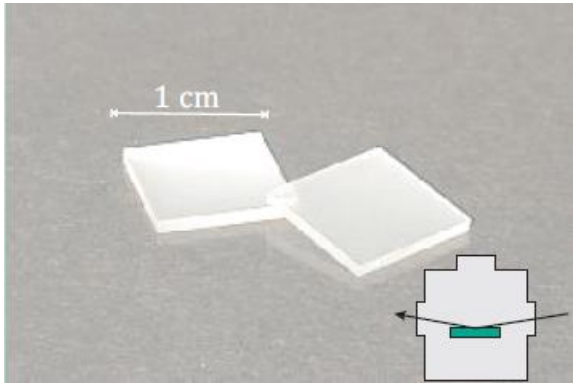
commercial powders



UHV-FTIR apparatus

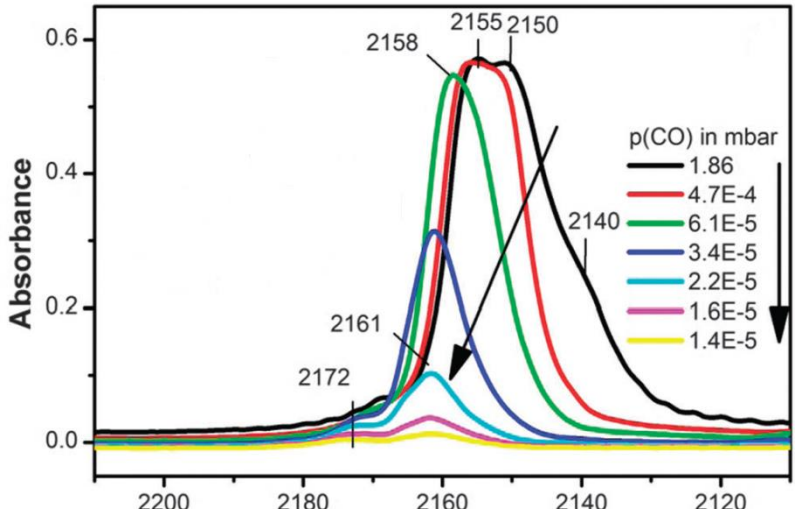


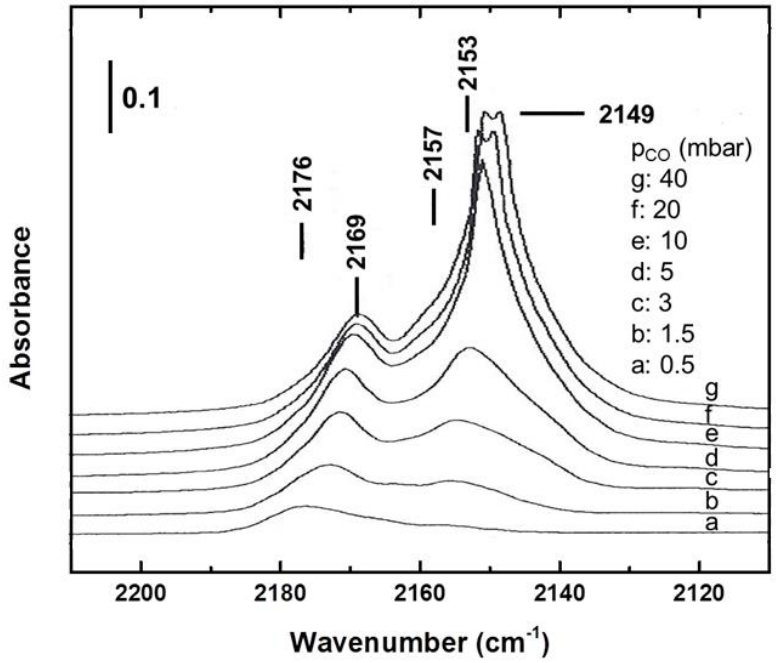
Powder IR measurements
in transmission mode

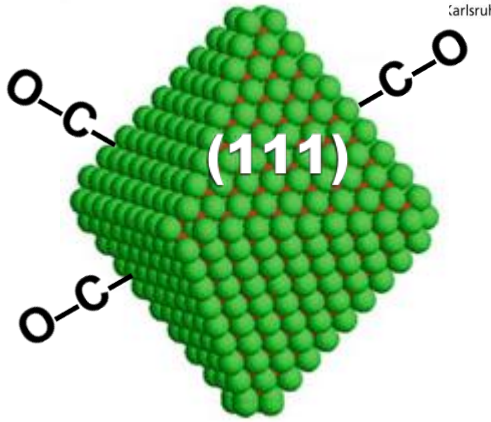


Oxide SXs IR measurements
in reflection mode

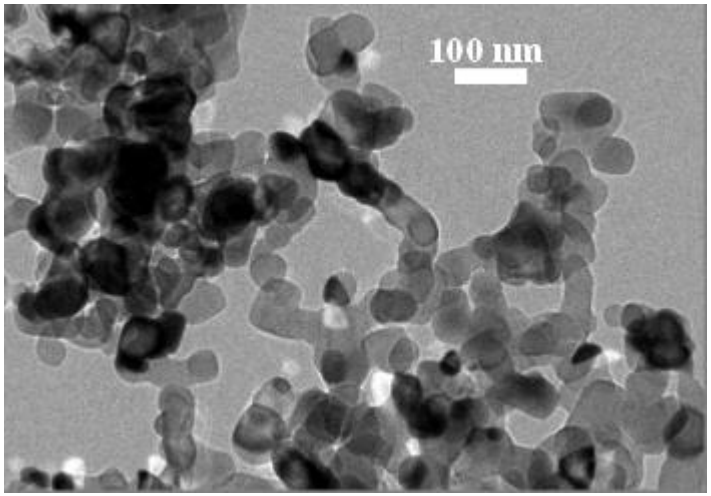
CO on ceria powders







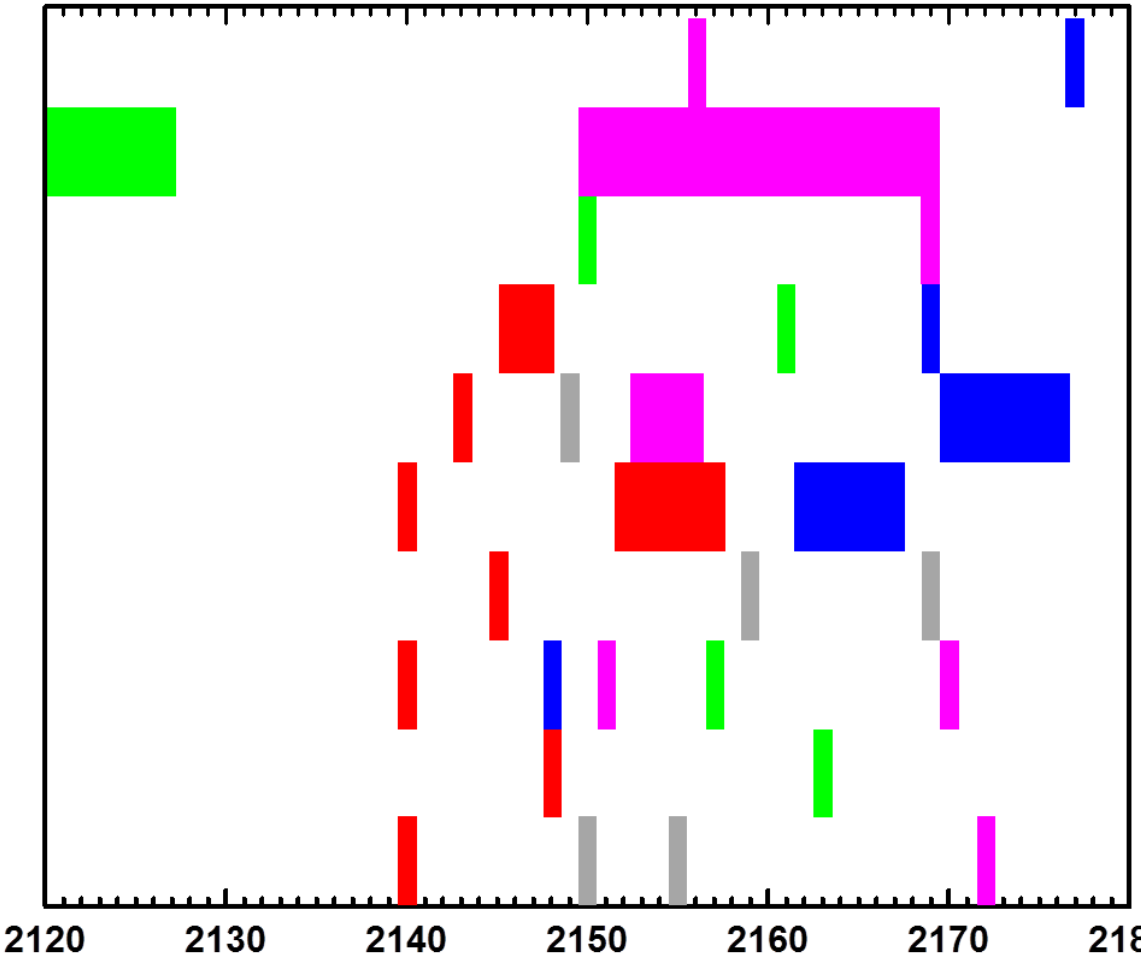
Wulff construction



How to assign the CO IR-bands?

R. Farra et al., *PCCP*, 2013, 15, 3454.
G. A. H. Mekhemer, M. I. Zaki, *Adsorpt. Sci. Technol.*, 1997, 15, 377.

Controversial assignments of CO IR-bands on ceria powders



J. Chem. Soc., Faraday Trans., 1989, 85, 929.

J. Chem. Soc., Faraday Trans., 1994, 90, 653.

J. Phys. Chem., 1986, 90, 3176.

J. Chem. Soc., Faraday Trans., 1996, 92, 1603.

Adsorpt. Sci. Technol., 1997, 15, 377.

Catal. Today, 1999, 50, 207.

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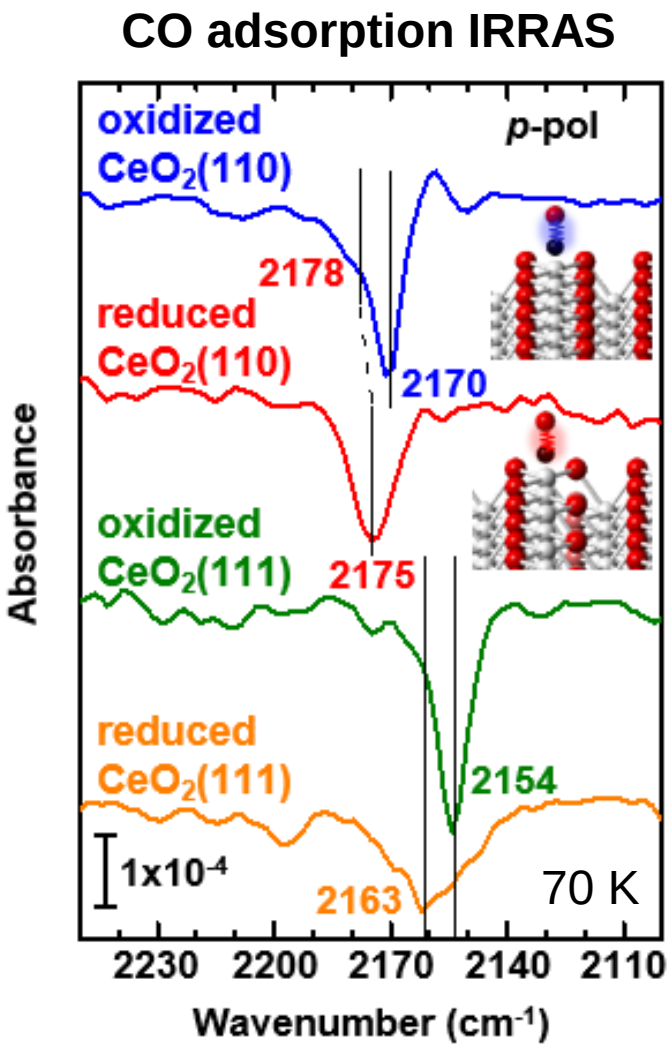
Appl. Catal. A: Gen., 2003, 252, 385.

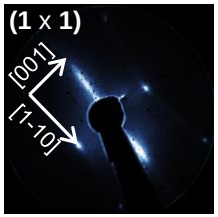
PCCP, 2005, 7, 187.

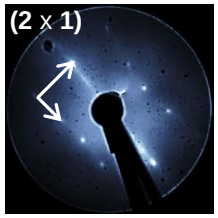
PCCP, 2013, 15, 3454.

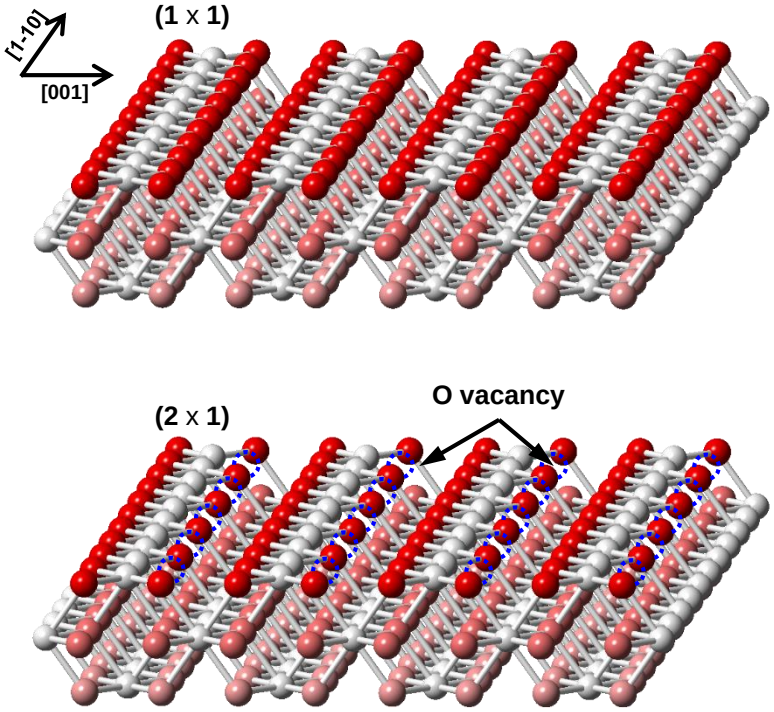
physisorbed CO | CO/Ce^{4+} | CO/Ce^{4+}_{cus} | CO/Ce^{3+} | other assignments

Surface structure of ceria (110) single crystal



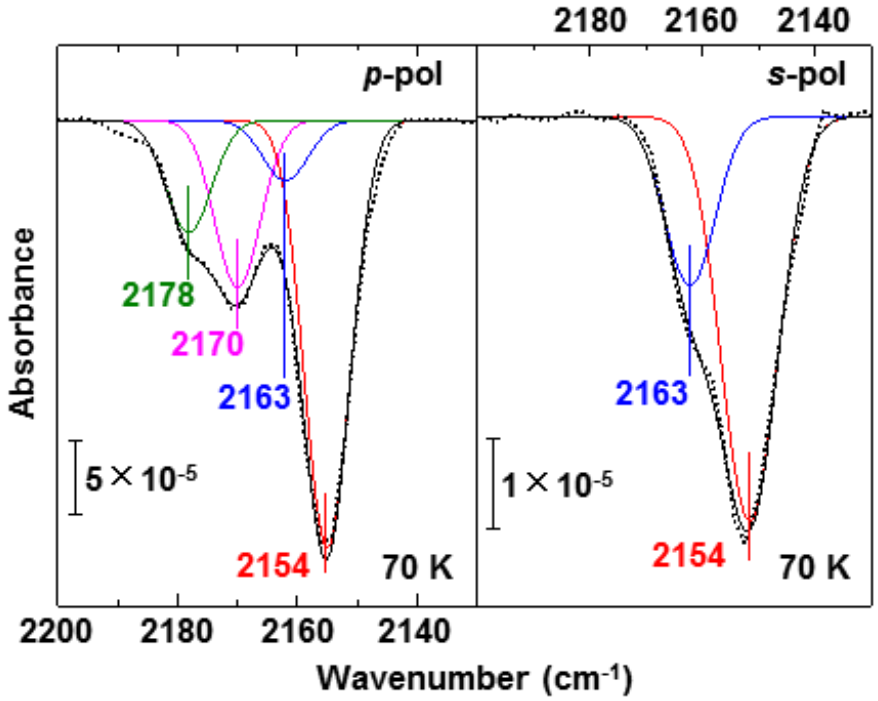


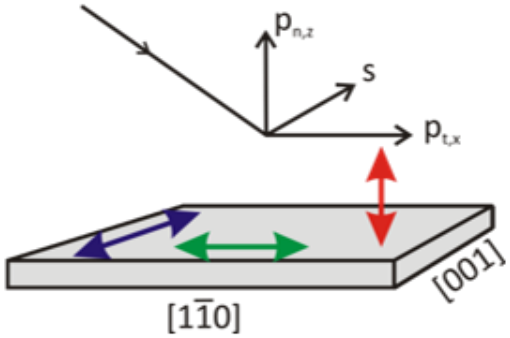


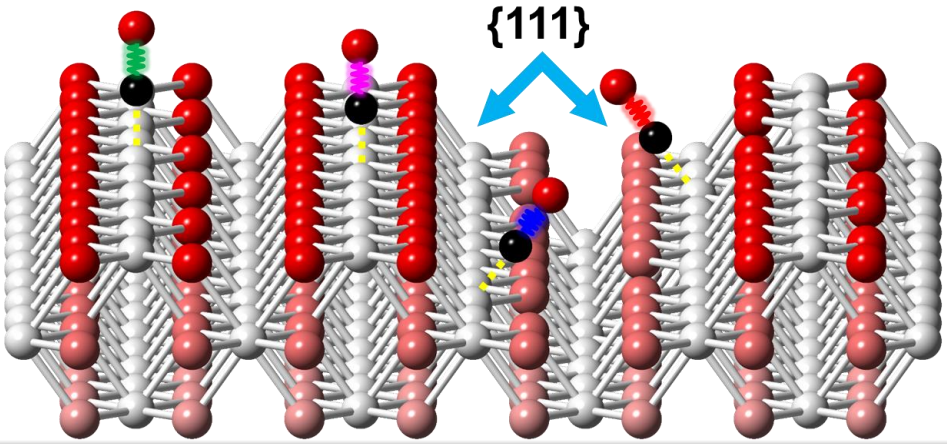


C. Yang, A. Trovarelli, Y. Wang, C. Wöll et al., *Angew. Chem. Int. Ed.*, 2017, 56, 375.
C. Yang, C. Wöll et al., *PCCP*, 2014, 16, 24165.

{111}-faceting of ceria (110) surface







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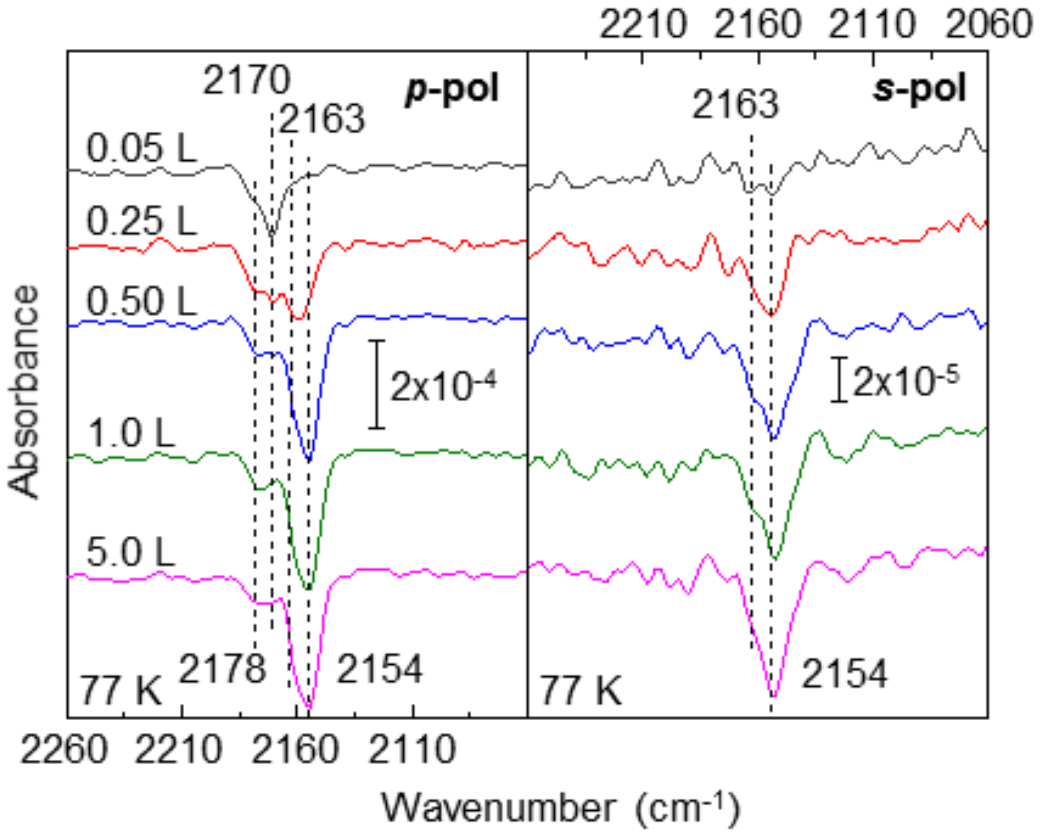
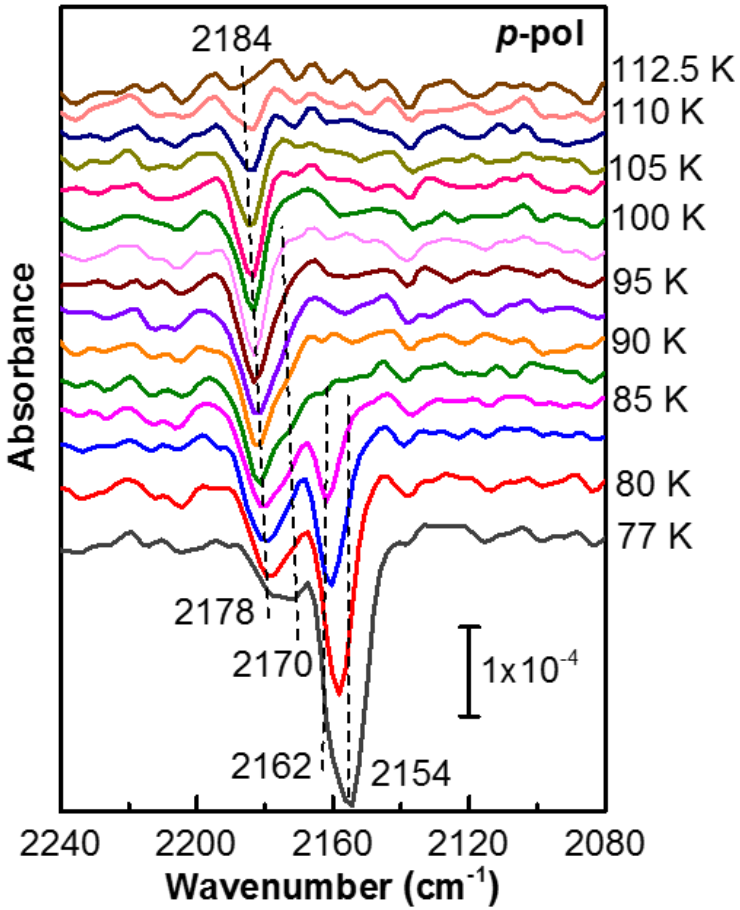
Spectral evolution of the faceted ceria (110) surface

with increasing CO coverage



with increasing temperature



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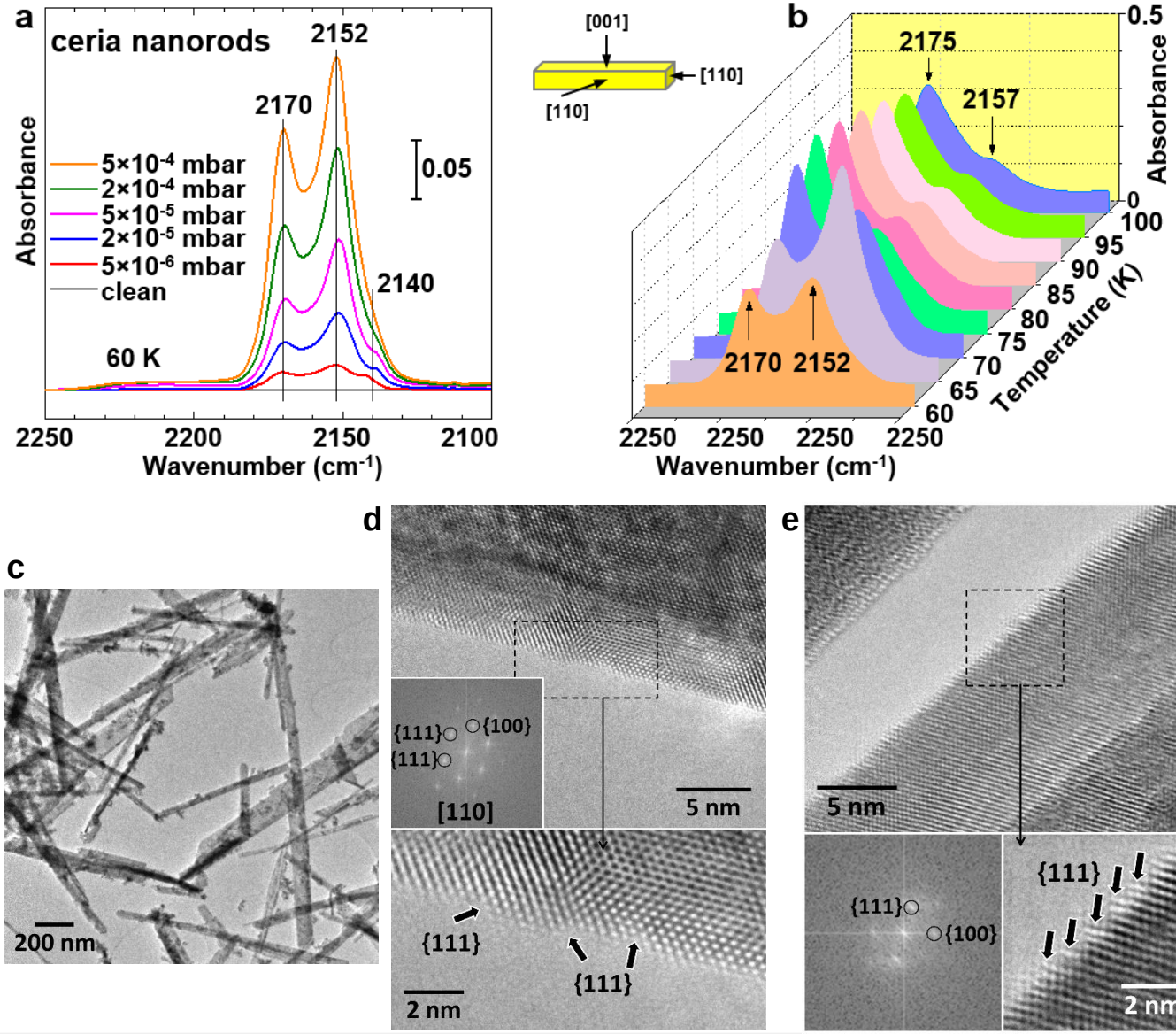
Surface structure of ceria nanorods



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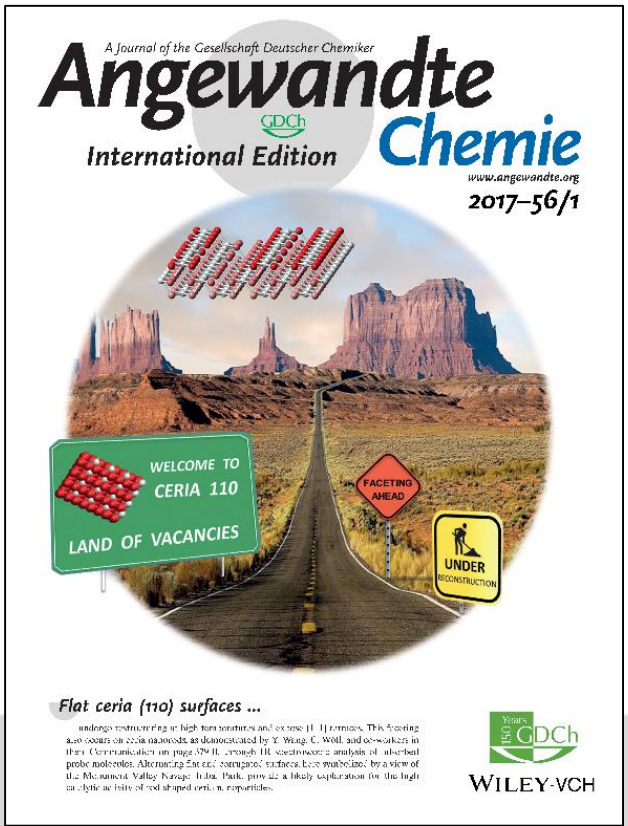
Summary

1. Using CO as probe molecule, IR spectroscopy can distinguish ceria surface orientations and probe oxygen vacancies.
2. We have presented, for the first time, a thorough IRRAS study on the atomic structure evolution of the catalytically most active CeO_2(110) single-crystal surface.
3. By calibrating the stretch frequency of adsorbed CO for various single crystal surfaces, we are able to demonstrate that the rod-shaped ceria NPs which previously were assumed to expose a (110)-terminated surface essentially restructure and the {111}-type faceting is an intrinsic property of the ceria (110) surface.



Science and Technology of Nanosystems (STN)

Helmholtz Research School Energy-Related Catalysis