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Surface Structure and Chemistry of CeO_2 Powder Catalysts Determined by Surface-Ligand Infrared Spectroscopy (SLIR)

Chengwu Yang, Hicham Idriss, Yuemin Wang, and Christof Wöll*

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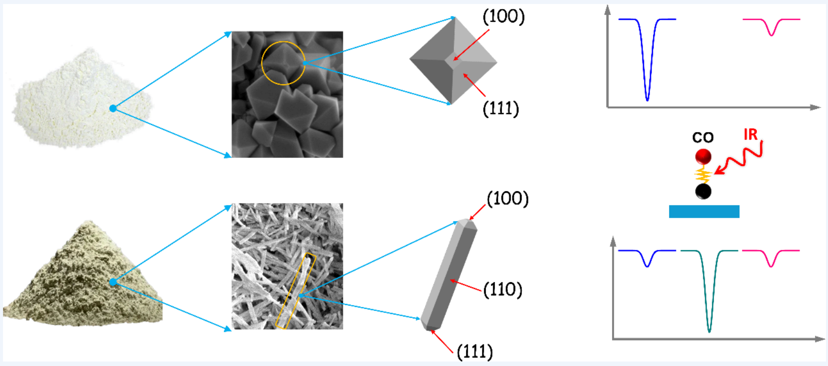

CONSPECTUS: Cerium is the most abundant rare earth element in the Earth's crust. Its most stable oxide, cerium dioxide (CeO_2, ceria), is increasingly utilized in the field of catalysis. It can catalyze redox and acid-base reactions, and serve as a component of electrocatalysts and even photocatalysts. As one of the most commonly used in situ/operando characterization methods in catalysis, infrared (IR) spectroscopy is routinely employed to monitor reaction intermediates on the surface of solid catalysts, offering profound insight into reaction mechanisms. Additionally, IR vibrational frequencies of probe molecules adsorbed on solid catalysts provide detailed information about their structure and chemical states. Numerous studies in the literature have utilized carbon monoxide and methanol as IR probe molecules on ceria particles. However, assigning their vibrational frequencies is often highly controversial due to the great complexity of the actual surface of ceria particles, which include differently oriented crystal facets, reconstructions, defects, and other structural variations. In our laboratory, taking bulk ceria single crystals with distinct orientations as model systems, we employed a highly sensitive ultrahigh vacuum (UHV) infrared spectroscopy system (THEO) to study the adsorption of CO and methanol. It turns out that the theoretical calculations adopting hybrid functionals (HSE06) can bring the theoretical predictions into agreement with the experimental results for the CO frequencies on ceria single crystal surfaces. The obtained frequencies serve as reliable references to resolve the long-standing controversial assignments for the IR bands of CO and methanol adsorbed on ceria particles. Furthermore, these characteristic frequencies allow for the determination of orientations, oxidation states and restructuring of exposed crystal facets of ceria nanoparticles, which is applicable from UHV conditions to industrially relevant pressures of up to 1 bar, and from low temperatures (∼65 K) to high temperatures (∼1000 K). We also used molecular oxygen as a probe molecule to investigate its interaction with the ceria surface, crucial for understanding ceria's redox properties. Our findings reveal that the localization of oxygen vacancies and the mechanism of dioxygen activation are highly sensitive to surface orientations. We provided the first spectroscopic evidence showing that the oxygen vacancies on ceria (111) surfaces tend to localize in deep layers. In addition, we employed N_2O as a probe molecule to elucidate the origin of the photocatalytic activity of ceria and showed that the photocatalytic activity is highly sensitive to the surface orientation (i.e., surface coordination structure). This Account shows that probe-molecule infrared spectroscopy serves as a powerful in situ/operando tool for studying the surface structure and chemistry of solid catalysts, and the knowledge gained through the "Surface Science" approach is essential as a crucial benchmark.

KEY REFERENCES

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probe molecule to determine the surface structures of ceria nanoparticles, based on the accurate reference data acquired from ceria single-crystal surfaces.

- Yang, C.; Yu, X.; Heißler, S.; Weidler, P. G.; Nefedov, A.; Wang, Y.; Wöll, C.; Kropp, T.; Paier, J.; Sauer, J. O_2 activation on ceria catalysts − The importance of substrate crystallographic orientation. *Angew. Chem. Int. Ed.* **2017**, *56*, 16399−16404.[2] This work presents the first IRRAS data on dioxygen activation on monocrystalline ceria surfaces, showing superoxo and peroxo species formed on reduced $CeO_2(110)$ and $CeO_2(100)$, but not on $CeO_2(111)$, offering insights into the location of O vacancies and O_2 activation.
- Yang, C.; Capdevila-Cortada, M.; Dong, C.; Zhou, Y.; Wang, J.; Yu, X.; Nefedov, A.; López, N.; Shen, W.; Wöll, C.; Wang, Y. Surface refaceting mechanism on cubic ceria. *J. Phys. Chem. Lett.* **2020**, *11*, 7925−7931.[3] This paper explores the surface structural evolution and catalytic activity of ceria nanocubes for CO oxidation, using $CeO_2(100)$ reference data to reveal the atomic-level restructuring processes that govern surface polarity compensation in ceria nanocubes.
- Caulfield, L.; Sauter, E.; Idriss, H.; Wang, Y.; Wöll, C. Bridging the pressure and materials gap in heterogeneous catalysis: A combined UHV, in situ, and operando study using infrared spectroscopy. *J. Phys. Chem. C* **2023**, *127*, 14023−14029.[4] In this work, the understanding of CO interactions with cerium oxide surfaces is advanced by bridging the so-called materials and pressure gaps. In particular, the proper removal of gas-phase contributions to DRIFTS data is discussed.

1. INTRODUCTION

Cerium is the most abundant rare earth element in the Earth's crust, about as common as copper.[5] Therefore, cerium does not fall into the category of "critical rare earths", i.e. it is not subject to supply risks. In their oxides, most rare-earth elements only have a valence of 3 and form sesquioxide, with the exception of cerium, which forms cerium dioxide (CeO_2).

CeO_2, also known as ceria, is an inexpensive and versatile material. Ceria has been used in various applications, including polishing powders, solid oxide fuel cells and, thanks to its biocompatibility, even in new fields like biology and medicine.[6] However, ceria's most renowned application is in heterogeneous catalysis.[5,7,8] The superior performance of ceria in catalysis is attributed to its diverse surface structures, remarkable redox properties, ability to store and release oxygen, and its unique acid-base characteristics. Ceria was first introduced into heterogeneous catalysis in 1976 by Ford Motor Company for use in three-way catalysts to control vehicle emissions.[9] This application remains ceria's most significant success in catalysis. The increasing interest in ceria for catalytic applications is evident, as over 50% of scientific papers since 2015 have focused on this area.[5]

Ceria is widely used in catalysts for various redox and acid-base reactions due to its activity and support capabilities. Additionally, as a wide bandgap oxide (5.5−6 eV),[10,11] it serves in electrocatalytic and photocatalytic applications.[12]

CeO_2 crystallizes in a fluorite structure with a face-centered cubic (fcc) unit cell (space group $Fm\bar{3}m$).[13] Cerium cations bond with eight O nearest neighbors while O anions bond tetrahedrally with four Ce neighbors. The low Miller-index surfaces (111), (100) and (110) exhibit varying stability and reducibility (oxygen vacancy formation). These surfaces represent three types of ionic crystal surfaces whose stability was categorized by Tasker.[14] $CeO_2(110)$ is a Type 1 surface with zero charge per layer due to balanced anions and cations. $CeO_2(111)$ is a Type 2 surface with a three-layer repeat unit (Ce layer between two O layers), resulting in zero net dipole moment. $CeO_2(100)$ is a Type 3 surface with alternately charged planes and a dipole moment perpendicular to the surface, requiring significant reconstruction to lower free energy.[13] A straightforward way to eliminate the dipole moment is to transfer half of the oxygen ions from the O-terminated surface to the Ce-terminated surface on the opposite side.[3] However, there are some studies that have proposed alternative reconstruction scenarios.[15,16] In fact, how the polar $CeO_2(100)$ surface is reconstructed depends upon the specific conditions to which the surface is subjected.

Numerous computational studies have examined the stability of these three low-index surfaces of CeO_2, consistently finding that their stability decreases in the order: (111) > (110) > (100).[18] Recent theoretical research shows that near-surface vacancy formation energies for similar vacancy spacings follow a different trend: (110) < (100) < (111), which does not intuitively follow from the surface energies scale of their nonreduced surfaces.[17] The removal of an O atom (e.g., by heating-induced formation of O_2) leads to the creation of an oxygen vacancy and leaves two electrons behind. These negative charges occupy low-lying empty Ce 4f electronic states, thus reducing two Ce^{4+} ions to Ce^{3+}, yielding two polarons. The preference of vacancies for surface or subsurface sites, as well as the preferred location of the associated Ce^{3+} polarons, are both facet- and concentration-dependent.[19]

Ceria is commonly used as a catalytic material in the form of nanostructured particles. Most modern analytical techniques for solid materials, such as microscopy, thermal analysis, diffraction/scattering, and spectroscopy,[20] allow routine characterization of nanostructured ceria catalysts. However, the particle structure usually exhibits great complexity: each particle can expose different crystal planes, contain various defects (e.g., steps, edges, oxygen vacancies, surface reconstructions, facets), and display varying oxidation states of surface Ce ions. These characterization methods provide either local (e.g., microscopies) or overall averaged (e.g., spectroscopies) information, making it challenging to establish a precise structure−activity relationship.

The "Surface Science" approach,[21] developed since the 1960s, utilizes well-defined macroscopic model catalysts such as single crystals, and employs highly sensitive surface analysis techniques, typically in ultrahigh vacuum (UHV) environments, to investigate catalyst surface structure, physicochemical properties, and fundamental catalytic processes. Experimental findings gained from surface science studies serve to validate the theoretical analysis, enabling extrapolation to real-world conditions and fostering an atomic-level understanding of catalytic systems. While the "Surface Science" approach has seen significant success, particularly with metal systems,[22,23] only a few surface science studies on bulk ceria single crystals—a dielectric substrate—have been successfully carried out using limited techniques such as scanning tunneling microscopy (STM),[24] atomic force microscopy (AFM),[25] low energy electron diffraction (LEED) and temperature-programmed desorption (TPD).[26]

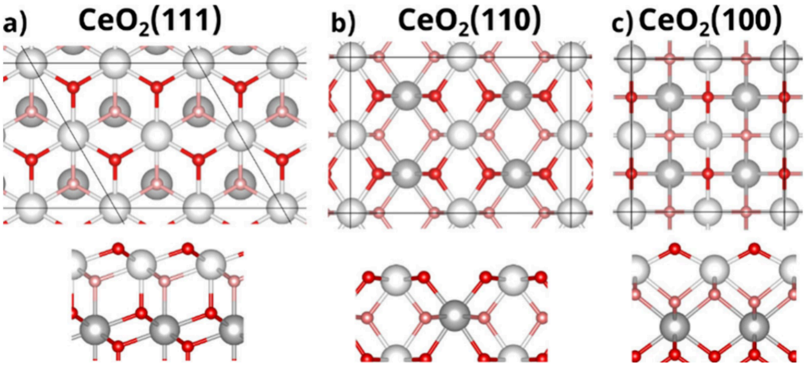

Figure 1. Top and side views of unrelaxed ceria surfaces: (a) (2 × 2)-(111), (b) (2 × 2)-(110), and (c) p(2 × 2)-(100) O-terminated. Color coding shows surface Ce (O) atoms in white (red) and deeper layer atoms in gray (light red). Reproduced with permission from ref 17. Available under a CC-BY 4.0 license.

Among the most informative techniques, infrared (IR) spectroscopy is particularly widely used today for in situ/operando characterization of catalysis.[27,28] Beyond tracking intermediate species to unveil reaction mechanisms, IR spectroscopy, when combined with probe molecules, offers insights into surface structure and chemical states.[29] There have been numerous IR studies on the use of probe molecules to discern the surface structure, oxidation state and acid-base properties of particulate ceria catalysts.[20] However, without referencing surface science studies, specifically reliable IR data from probe molecules adsorbed on well-defined ceria single crystals, accurately assigning the many observed vibrational bands in ceria particles remains challenging and prone to misassignment.

Infrared Reflection Absorption Spectroscopy (IRRAS) is a variant of infrared spectroscopy suitable for studying adsorbates on planar model surfaces, proving highly effective in revealing the structure, physicochemical properties and chemistry of metal single crystal surfaces. This technique has been extensively applied to nearly all metals across the periodic table.[30] However, its application to metal oxides has been limited due to the very low reflectivity of dielectric substrates in the infrared range. Kattner and Hoffmann concluded that oxides' optical properties reduce the signal-to-noise ratio (S/N) by one to 2 orders of magnitude compared to metals, posing a significant challenge for acquiring IR spectra from oxide single crystal surfaces in reflection geometry.[31] As a result, the first reported IRRAS study of a molecular adsorbate on a metal oxide single crystal surface did not appear until 1999, conducted by Hayden and colleagues.[32] They investigated the formate species generated by the dissociative adsorption of formic acid on a rutile-$TiO_2(110)$ surface using IRRAS. It would take another 10 years for further advancements in IRRAS studies using other probe molecules on this essential model substrate.[33] It was only in 2014 that our group reported the first IRRAS results of probe molecule (CO) adsorption on well-defined surfaces of ceria single crystals.[34]

Alternatively, the use of a special type of model system, i.e. ceria thin films epitaxially grown on suitable metal substrates, can address the challenges of applying IRRAS.[13,35] Prior to 2014, IRRAS research on adsorbates on macroscopic ceria surfaces exclusively focused on such thin films grown on metallic substrates.[13] In this case, the supporting metal acts as a mirror, greatly enhancing the reflectivity. Over the decades, ceria thin films have proven successful, and surface analysis techniques involving charged-particle beams are also applicable. However, challenges remain, such as the inability to successfully grow (110)-oriented ceria films and the difficulty in fabricating low-defect-density films due to lattice mismatches with the oxide on the supporting metal. Particularly for thin metal oxide films (especially those thinner than 10 nm), there is the possibility of charge transfer from the metal substrate to the film surface, potentially influencing surface properties,[36] as demonstrated by our previous studies on ZnO thin films.[37−39] Finally, the supporting metal can shield the component of the incident IR light's E vector that is parallel to the surface, preventing the study of adsorbate vibrations along the substrate.[40] There are only few IRRAS studies available for CO adsorbed on ceria thin films grown on metal substrates;[41] results for CO on fully oxidized ceria thin films with (111) orientation have been reported only recently.[42]

Since 2014, we have conducted extensive investigations into the adsorption of various probe molecules on ceria single crystals of different orientations using an advanced ultrahigh vacuum infrared spectroscopy (UHV-FTIRS) apparatus, known as THEO.[43,44] Its innovative design enables recording IRRAS data at grazing incidence on model oxide single crystals and performing transmission IR measurements on industrially relevant oxide powders.[45] THEO has consistently demonstrated exceptional sensitivity and stability, enabling us to reliably obtain high-quality IR spectra. Initially, we studied the adsorption of the most commonly used infrared probe molecules, CO and methanol, on ceria surfaces.[34,46] With the aid of the precise theoretical calculations, the experimental frequencies obtained serve as a reliable reference, thus resolving long-standing debates. Furthermore, based on these characteristic frequencies, the orientations and oxidation states of the exposed crystal facets of ceria nanoparticles can be elucidated, which is applicable across a wide range of conditions, from UHV to industrially relevant pressures up to 1 bar and from low to high temperatures.[4] We also used molecular oxygen as a probe molecule to study the interaction between the ceria surface and dioxygen, which is key to understanding the redox properties of ceria. Our findings revealed that the localization of oxygen vacancies on crystal surfaces and the mechanism of dioxygen activation are dependent on the surface orientation.[2] Furthermore, employing nitrous oxide (N_2O) as a probe molecule has allowed us to elucidate the origin of the photocatalytic activity of ceria.[47]

When it comes to techniques suited for studying both single crystal bulk samples as well as technologically relevant powder samples, SLIR (surface ligand IR spectroscopy) is the most prevalent.[29] Although scanning probe techniques such as AFM and STM have been applied to ceria single crystals and oxide thin films,[24,48,49] their application to ceria powder samples remains unexplored.

2. CARBON MONOXIDE (CO) ADSORPTION

In heterogeneous catalysis, powdered ceria materials are predominantly used, comprising nano/micron-sized particles that expose facets with varying crystallographic orientations. These surfaces exhibit distinct structures (see Figure 1), varying reducibility, i.e. oxygen vacancy formation, and consequently demonstrate different chemical activities. The use of CO as a probe molecule in infrared spectroscopy has proven highly sensitive in identifying oxide surface structures and detecting surface oxygen vacancies. Previously, numerous IR studies have investigated ceria powder samples exposed to CO under static and operando conditions to gain detailed insights into reaction mechanisms. However, due to the lack of IR data from CO adsorption on well-defined ceria single crystals as a reference, the assignments of the normally broad and overlapping CO bands observed for ceria particles are debatable and sometimes arbitrary. Figure 2 summarizes IR band assignments from representative literature for CO adsorbed on ceria particles,[50−58] with colored bars indicating different assignments and bar width representing bandwidth. This review provides theory-supported reference data that will enable reliable characterization of the chemical state of ceria nanoparticles in the future.

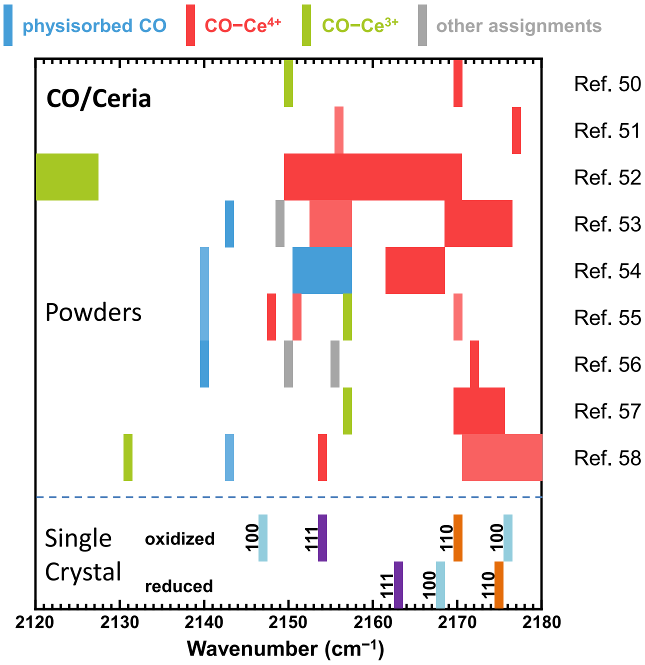

Figure 2. Summary of IR band assignments from representative literature for CO adsorbed on ceria particles.[50−58] The single crystal data reported by our group were presented below as a reference.

2.1. CO Adsorption on Ceria Single Crystal Surfaces

To address the controversies over IR band assignments of CO adsorbed on ceria particles, we systematically conducted polarization-dependent IRRAS experiments on all three low-index ceria (111), (110), and (100) single-crystal surfaces, both oxidized and reduced, at low temperatures (∼70 K). The results are summarized in Figure 3. For ceria (111) surfaces treated with 1 keV Ar^+ sputtering and annealed at 800 K in either an O_2 atmosphere or UHV (for reduction), CO adsorption produced a prominent band in p-polarization at 2154 and 2163 cm^{-1} on saturated surfaces. These represent shifts of +11 and +20 cm^{-1} from the gas phase CO (2143 cm^{-1}). Notably, the 2154 cm^{-1} band aligns well with findings from other studies on fully oxidized ceria (111) thin films.[42] Similar processes on (110) surfaces showed a strong negative band at 2170 cm^{-1} (oxidized) and 2175 cm^{-1} (reduced). On oxidized (100) surfaces, CO showed a strong band at 2176 cm^{-1}, with a shoulder at 2168 cm^{-1} and a weaker peak at 2147 cm^{-1}. Reducing the (100) surface further shifted the main band from 2176 to 2168 cm^{-1}, while the 2147 cm^{-1} band persisted. The s-polarized IRRAS data only displayed a weak CO feature on the (111) surface and none on the (110) and (100) surfaces, indicating that CO on all tested surfaces adopts an upright or slightly tilted orientation, confirming theoretical predictions.

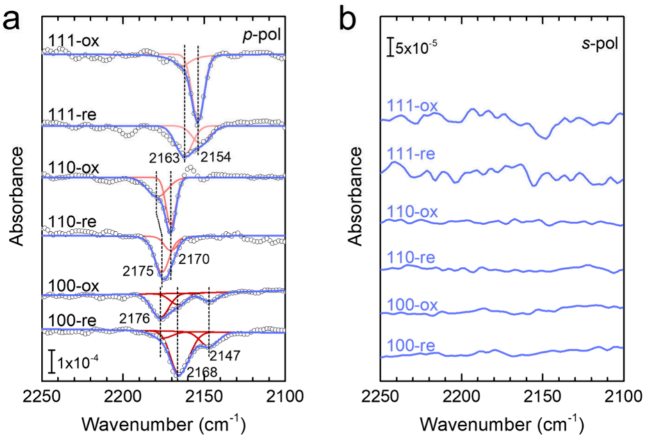

Figure 3. IRRAS data recorded for different polarizations for one monolayer (ML) of CO adsorbed on oxidized and reduced (111), (110), and (100) CeO_2 at 70 K: (a) p-polarized spectra; (b) s-polarized spectra. Reproduced with permission from ref 17. Available under a CC-BY 4.0 license.

The complete range of CO stretch frequencies on various low-index ceria surfaces offers a unique chance to confirm electronic structure calculations. For $CeO_2(111)$, reasonable agreement was initially achieved with the DFT + U method. However, significant discrepancies were noted for the $CeO_2(110)$ surface, where experimental blue-shifted signals diverged from DFT + U calculations that showed an unexpected red-shift. This mismatch was linked to methodological limitations. Adopting hybrid functionals (HSE06) corrected this, aligning theoretical predictions with experimental results for CO frequencies on all low-index CeO_2 surfaces, both oxidized and reduced (see Table 1).[17]

Note that the particular properties of dielectric surfaces give rise to various surprising and often counterintuitive experimental observations in IRRAS, such as the change of sign of adsorbate-related IRRAS bands and polarization-dependent shifts of vibrational bands. In addition, for very small particles further shifts of vibrational frequencies are expected.[59] Since a discussion of these aspects goes beyond the scope of this article mainly focusing on powder particles, the reader is referred to a recent paper on this subject by some of the present authors.[60]

2.2. CO Adsorption on Ceria Nanocrystals

Ceria nanocrystals with different morphologies can be synthesized by hydrothermal method without the need for

Table 1. Data from Calculations Using Density Functional Theory (DFT) for the Adsorption of 1 ML CO on the Three Low-Index Oxidized and Reduced CeO_2 Surfaces[a]

Method	CO Site	E_{ads} (eV)	ν (cm^{-1})	Method	Vacancy Site	E_{ads} (eV)	ν (cm^{-1})
	$CO/CeO_2(111)$ (1 × 1)				$CO/CeO_{2-x}(111)$ (2 × 2)		
IRRAS			2154	IRRAS			2163
HSE06 (PBE+U)	Top	−0.09 (−0.03)	2157 (2144)	HSE06 (PBE+U)	VS/VSS	−0.18/−0.11 (−0.19/−0.13)	2167/2159 (2145/2145)
	$CO/CeO_2(110)$ (1 × 1)				$CO/CeO_{2-x}(110)$ (2 × 2)		
IRRAS			2170/2160	IRRAS			2175
HSE06 (PBE+U)	Top	−0.15 (−0.16)	2165 (2151)	HSE06 (PBE+U)	VS	−0.14 (−0.17)	2168 (2146)
	Tilt.1	−0.20 (−0.22)	2145 (2120)				
	Tilt.2	−0.19 (−0.21)	2150 (2130)				
	$CO/CeO_2(100)$ (1 × 1)				$CO/CeO_{2-x}(100)$ (2 × 2)		
IRRAS			2176/2168/2147	IRRAS			2168/2147
HSE06 (PBE+U)	Bridge	−0.29 (−0.31)	2176 (2152)	HSE06	VS	−0.27 (−0.32)	2172 (2157)
	Top	−0.06 (−0.04)	2151 (2149)		VSS	−0.22 (−0.23)	2172 (2155)

[a] The CO adsorption site, the position of the oxygen vacancy [surface (VS)/subsurface vacancy (VSS)], the adsorption energy (E_{ads} in eV) and vibrational frequency shift ($\Delta\nu$ in cm^{-1}) are indicated. Reproduced with permission from ref 17. Available under a CC-BY 4.0 license.

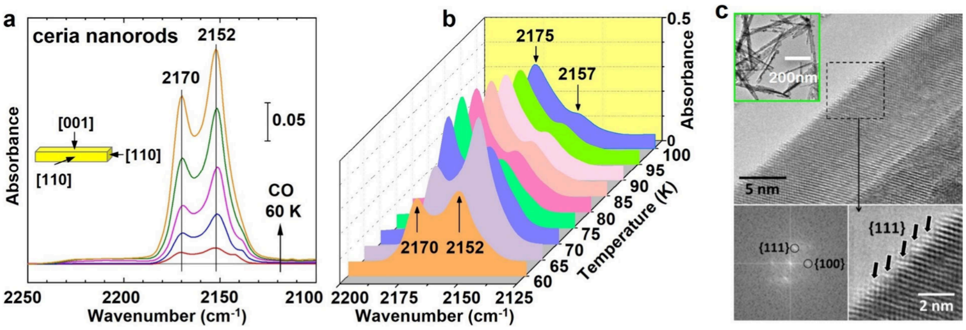

Figure 4. (a,b) Surface analysis of ceria nanorods using IR post-CO adsorption included (a) UHV-FTIR spectra after various CO exposures at 60 K; (b) spectra after heating to higher temperatures. (c) High-resolution HRTEM images displayed clear {111}-facets on the (110) plane of CeO_2 nanorods. A general view of rod-shaped CeO_2 nanoparticles is displayed in the inset. Reproduced with permission from ref 1. Copyright 2017 Wiley.

organic structure-directing agents. Since these uniform nanocrystals can predominantly expose facets with different crystallographic orientations, e.g. nanooctahedra mostly exposing {111} facets, nanocubes mostly exposing {100} facets, and nanorods mostly exposing {110} and {100} facets, they have extensively served as model catalysts for investigating structure-performance relationships in ceria-catalyzed reactions.[61] Unlike oxide model catalysts based on single crystals and thin films studied under UHV conditions, these nanocrystals represent a new class of model catalysts that can be examined under the same conditions as working oxide catalysts. The surface structures of these oxide nanocrystals can be characterized by high-resolution transmission electron microscopy (TEM). However, the microscopic techniques provide only local information, and a significant number of images per sample are required to develop quantitative data. Therefore, to complement microscopic techniques, probe molecule infrared spectroscopy is preferred, offering insights into the surface chemistry and catalytically active properties of these oxide nanocrystals.

In the same UHV-IR apparatus (THEO), but operated in transmission mode,[44] we again used CO as an infrared probe molecule to investigate the surface structure of ceria nanorods.[1] Figure 4a shows the corresponding IR data recorded at 60 K, revealing two dominant CO vibrational bands at 2170 and 2152 cm^{-1}. These bands are assigned to CO bound to Ce^{4+} sites within the (110) and (111) surface regions, respectively, based on comparisons with IRRAS results from well-defined ceria single-crystal surfaces (see Figure 3). The assignment was further supported by the temperature-dependent IR data (Figure 4b), which show spectral evolution of various CO species with distinct binding energies. These spectroscopic findings directly reveal that ceria nanorods expose a large number of (111)-oriented surface regions resulting from faceting of the (110) planes, a conclusion corroborated by high-resolution TEM (see Figure 4c). These observations prompt consideration of whether these structural features contribute to the enhanced catalytic performance typically observed in such ceria nanoparticles.

IR spectra for CO on ceria nanocubes revealed similar frequencies between reduced and oxidized states and $CeO_2(100)$ surfaces (see Figure 5).[3] After heating at 750 K, three IR bands appeared at 2174, 2166, and 2149 cm^{-1}, linked to the O-terminated (2 × 2) ceria (100) surface. Further annealing at 900 and 1000 K produced typical CO bands at 2154 and 2160 cm^{-1} from {111} facets, indicating significant surface restructuring, mirroring monocrystalline results. This is supported by HRTEM/STEM images showing surface refaceting of ceria nanocubes (Figure 5c). The restructuring, driven by {100} facet instability, enhances catalytic activity through increased O vacancies and defect sites, critical for CO oxidation (Figure 5d).

In a recent work, we demonstrated that the information obtained for single crystals can be used in a straightforward fashion to interpret high pressure DRIFTS (diffuse reflectance infrared Fourier transform spectroscopy) data recorded for ceria

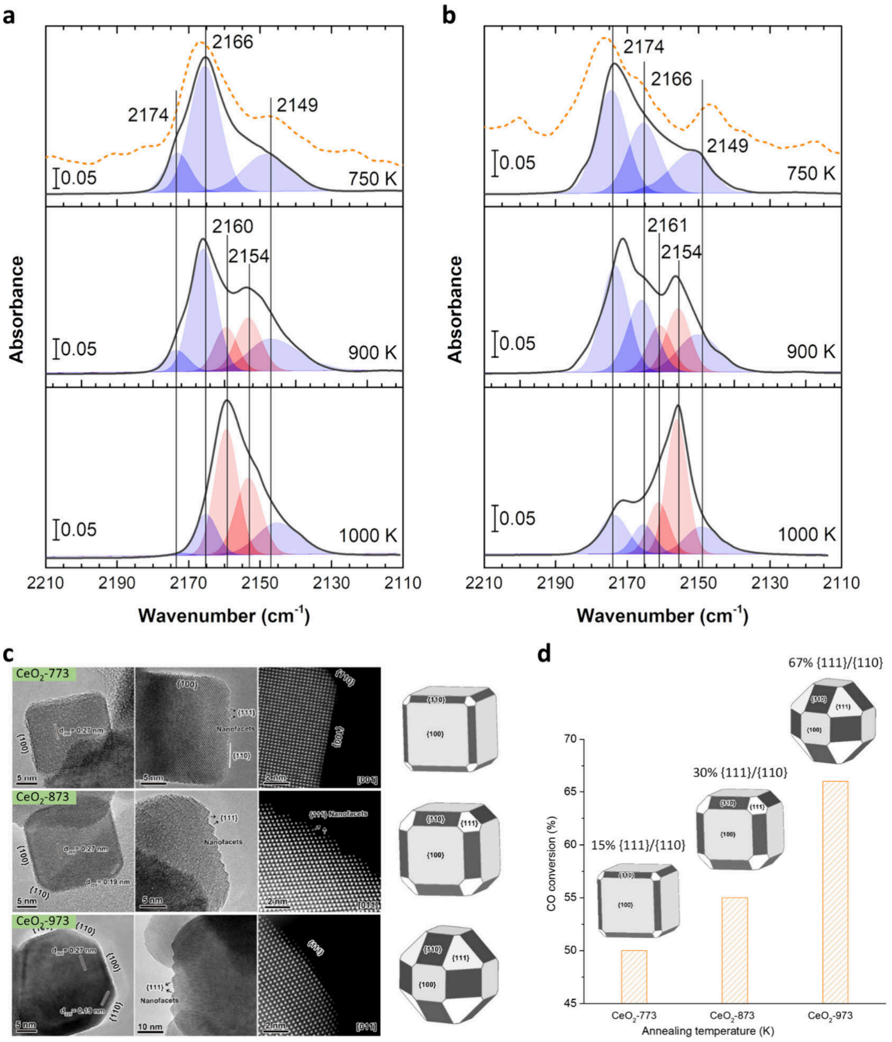

Figure 5. (a,b) Structural evolution of ceria nanocubes probed by IR after CO adsorption. (a) Deconvoluted FTIR spectra show CO adsorption on ceria nanocubes heated to specified temperatures (reduced) and (b) exposed to O_2 at low temperatures, then warmed to 300 K (oxidized). For comparison, dashed curves in the corresponding IRRAS data (Figure 3) depict CO on O-terminated (2 × 2) $CeO_2(100)$ single-crystal surfaces with reversed signs. (c) Structural evolution of ceria nanocubes visualized by HRTEM/STEM. (d) Evaluation of the catalytic activity for CO oxidation. Reproduced with permission from ref 3. Copyright 2020 American Chemical Society.

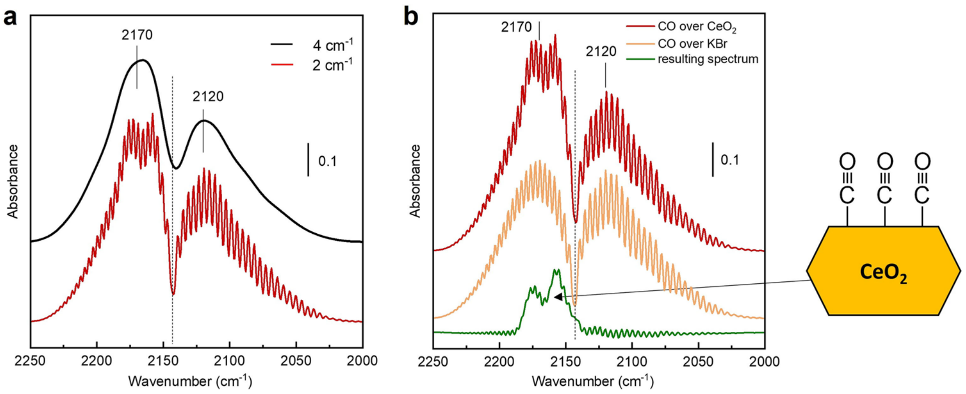

Figure 6. (a) Raw DRIFTS data for CeO_2 nanoparticles were recorded at a CO pressure of 1 bar and 295 K, featuring low (4 cm^{-1}, top) and high (2 cm^{-1}, bottom) resolution. (b) Increasing the resolution to 2 cm^{-1} allowed for clear observation of the low intensity signals of CO bound to ceria surfaces. This was achieved by applying a normalization/subtraction scheme, where the DRIFT spectrum recorded for a reference powder (KBr, middle) is subtracted from the spectrum of the powder catalyst (top). The resulting difference spectrum (bottom) exclusively exhibits adsorbate vibrations, including various CO species adsorbed on CeO_2 particles. Reproduced with permission from ref 4. Copyright 2023 American Chemical Society.

powders at CO pressures of one bar.[4] By applying an optimized experimental setup and a novel normalization/subtraction scheme for in situ/operando DRIFTS data, the intense gaseous CO rovibrational bands can be completely removed, thus allowing for an unambiguous identification of vibrational bands of CO adsorbed on bare ceria powder particles under ambient conditions (Figure 6). On the basis of the comprehensive IRRAS data recorded for all low-indexed ceria single crystals under UHV conditions (Figure 3) and of DFT results using hybrid functionals (Table 1),[17] all CO bands in the DRIFTS data could be assigned to specific crystallographic orientations.

This capability permits not only the observation of surface structural transformations in ceria particles at high pressures and temperatures but also the real-time monitoring of the particles' reduction process in a reducing (CO) atmosphere.

3. METHANOL ADSORPTION

Methanol, the simplest alcohol, is a common probe for characterizing active sites on oxide surfaces through IR spectroscopy, which is widely used to examine methanol interactions with ceria nanoparticles and films. The C−O stretching mode of methanol on CeO_2 typically ranges from 1000 to 1200 cm^{-1}, indicating molecular and/or dissociative adsorption. Earlier studies on ceria powders suggested that the redshift in the methoxy C−O stretch correlates with the number of Ce cations coordinating it, with bands at 1108, 1065, and 1015 cm^{-1} linked to monodentate, bidentate, and tridentate methoxide species, respectively.[62] However, this assignment has been reevaluated based on IR bands from methanol on defined $CeO_2(110)$ and $CeO_2(111)$ monocrystal surfaces, supported by a comprehensive set of DFT calculations.[46]

Methanol adsorption on the fully oxidized $CeO_2(110)$ surface shows a significant 1108 cm^{-1} band in IRRAS, linked to monodentate methoxy species bound to $Ce^{4+}{}_{6c}$ ions, supported by theoretical analysis (Figure 7). CD_3OD adsorption exhibits a 1060 cm^{-1} peak, aligning with expected isotope shifts (Figure 7b). On the $CeO_2(111)$ surface, IRRAS detects three complex bands at 87 and 120 K, with two main bands at 1085 and 1060 cm^{-1}, shifting to 1040 and 1020 cm^{-1} under CD_3OD due to isotope effects. A minor 1108 cm^{-1} feature corresponds to methoxy on (110) facets at $CeO_2(111)$ step edges. Molecular dynamics simulations suggest these bands represent a methanol monolayer of H-bonded methoxide and molecular methanol at various coverages.[46] These results challenge the simple correlation between methoxy CO stretch redshift and cerium cation coordination previously proposed.

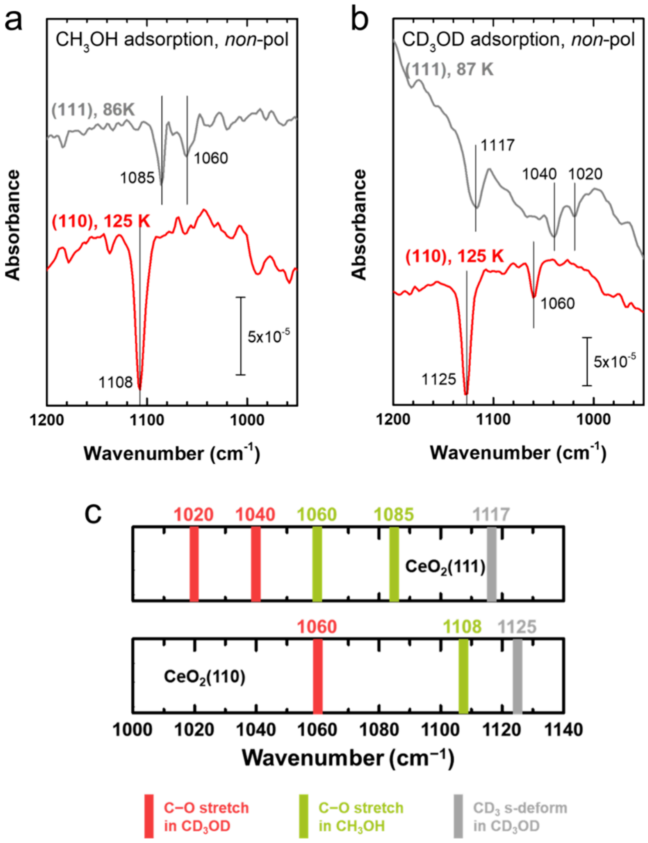

Figure 7. IRRAS data of 1 ML (a) CH_3OH and (b) CD_3OD adsorption on the oxidized (111) and (110) ceria surfaces; (c) vibrational frequencies and band assignments of methanol on $CeO_2(111)$ and $CeO_2(110)$. Reproduced with permission from ref 46. Copyright 2016 Elsevier.

4. MOLECULAR OXYGEN (O_2) ADSORPTION

Ceria stands out as one of the most catalytically active materials for redox reactions, owing largely to its low formation energy for oxygen vacancies. The creation of an oxygen vacancy is accompanied by the formation of two Ce^{3+} polarons. The interaction of molecular oxygen with the reduced ceria surfaces, i.e. the adsorption, activation, and subsequent dissociation of oxygen molecules, is a particularly important topic. In the initial step of oxidation catalysis, substrate O atoms typically oxidize the reactant, such as CO or organics. The vacancies created at the oxide surface must subsequently be replenished by activating and dissociating gaseous O_2, thus closing the catalytic cycle. Although this Mars-van Krevelen mechanism is generally accepted to describe the reactions on redox catalysts, atomistic insight into the processes remains limited. Electron paramagnetic resonance (EPR) spectroscopy, alongside Raman and infrared spectroscopies,[20] has provided significant insights into the activation of surface molecular oxygen by electron transfer from the substrate, particularly in ceria nanoparticles. Previous studies on powders have detected superoxo and peroxo species, yet due to the complex surface structures exposed by ceria particles, assigning these vibrational bands to specific adsorption sites has remained challenging. This would be a key requirement for the validation of theoretical approaches.

In our recent study, we analyzed O_2 activation on all low-index CeO_2 surfaces using systematic, polarization-resolved IRRAS.[2] IRRAS data after molecular O_2 adsorption at 110 K on these surfaces, shown in Figure 8, indicate no detectable vibrations for fully oxidized samples, as expected given O_2's IR inactivity. However, reduced (110) and (100) surfaces showed clear vibrational bands at ∼1130 and 885 cm^{-1} in p-polarized IR, assigned to superoxo ($O_2^{\bullet-}$) and peroxo (O_2^{2-}) species, respectively, from comparisons with Raman data and theoretical predictions (Figure 8b). The 885 cm^{-1} band was absent on the (100) surface due to its unique peroxo binding structure. Contrarily, no superoxo or peroxo bands appeared on the more stable $CeO_{2-x}(111)$ surface, suggesting deeper oxygen vacancies, aligning with theoretical expectations.[19] These findings underscore the variations in oxygen vacancy locations and O_2 activation across different ceria surfaces, enhancing our understanding of their structural properties.[2]

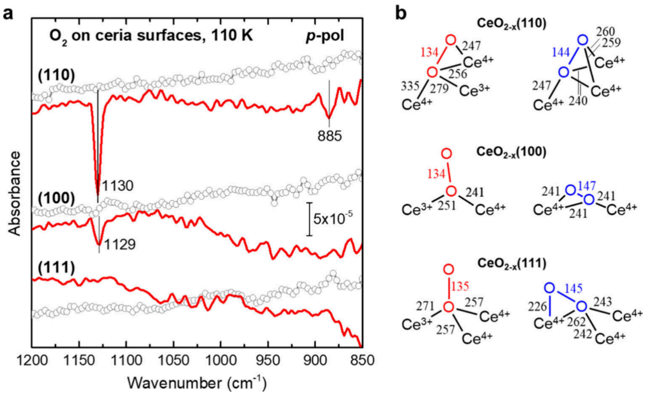

Figure 8. (a) Interactions of dioxygen with ceria surfaces were studied under oxidized (black, open circle) and reduced (red, solid line) conditions using p-polarized IRRAS after O_2 exposure at 110 K on the (111), (110), and (100) surfaces. (b) Atomic structures and bond lengths of superoxide (red) and peroxide (blue) species formed on the reduced CeO_{2-x}(110), CeO_{2-x}(100), and CeO_{2-x}(111) surfaces are detailed. Reproduced with permission from ref 2. Copyright 2017 Wiley.

5. NITREOUS OXIDE (N_2O) ADSORPTION—THE PHOTOREACTIVITY OF CERIA

Ceria is well-known for its role as a catalyst or support in (thermal) heterogeneous catalysis. It has also attracted attention because oxygen-deficient CeO_2 (CeO_{2-x}) in its polycrystalline form absorbs visible light and therefore has the potential of being one of the future multicomponents photocatalysts for light harvesting to chemicals. In that regard, fundamental studies conducted on well-defined metal oxide photocatalysts are scarce, in particular those disentangling structural (such as surface orientation) effects from electronic effect (such as cation oxidation sates).

Recently, we have conducted a comprehensive study using polarization-dependent IRRAS to explore the activity of macroscopic monocrystalline ceria (110) and (111) surfaces under photo excitation with a probe reaction: the direct photoinduced decomposition of nitrous oxide (N_2O) at low temperatures.[47,63] It was found that under UV illumination, the intensity of the asymmetric stretching bands of N_2O adsorbed on fully oxidized ceria (110) and (111) surfaces remained nearly constant, indicating minimal catalytic activity while on the same single crystals when they are deficient in oxygen a non-negligible activity occurred. Moreover, the CeO_{2-x} (110) single crystal was found to be more active than the CeO_{2-x}(111) single crystal. Figure 9a displays p-polarized IRRA spectra of 1 ML N_2O on the CeO_{2-x}(111) surface at 120 K, showing positive and negative bands at approximately 2231 and 2248 cm^{-1}, respectively, due to the asymmetric stretching of N_2O. Figure 9b captures similar data after N_2O adsorption and reaction on CeO_{2-x}(110) under the same conditions. Following the identification of distinct N_2O species on these surfaces, their photochemical decomposition was explored by tracking changes in vibrational band intensity under UV irradiation. Figure 9c plots the logarithmic ratio of initial to time-specific IR signals ($\ln(C_0/C_t)$) against UV exposure time. The reduced ceria (110) surface showed a photoreaction cross-section of about 5×10^{-19} cm^2, indicating a 2.5 times faster decay than CeO_{2-x} (111), possibly due to more efficient polaron hopping on the (110) surface. This study is among the few employing IRRAS for photochemical analysis on oxide single crystals.

6. CONCLUDING REMARKS

Over the past decade, we have demonstrated the capability of determining the surface structure and chemistry of model CeO_2 catalysts using various probe molecules in a highly sensitive ultrahigh vacuum infrared spectroscopy system (THEO). Specifically, we can use CO, O_2, and methanol to identify the crystallographic orientation and the location of surface/subsurface oxygen vacancies of ceria. The polarization-resolved IRRAS data obtained from ceria single crystal models can also be used to validate the theoretical calculations and thus to resolve the long-standing band assignment debates over actual ceria particle systems. Notably, our studies marked the first direct observation of superoxo and peroxo species on ceria (110) and (100) single crystals, while providing spectroscopic evidence that oxygen vacancies on the (111) surface are predominantly located in the subsurface layer. Additionally, our systematic investigation with N_2O as a probe molecule has contributed to understanding the origins of ceria's photocatalytic activity. By

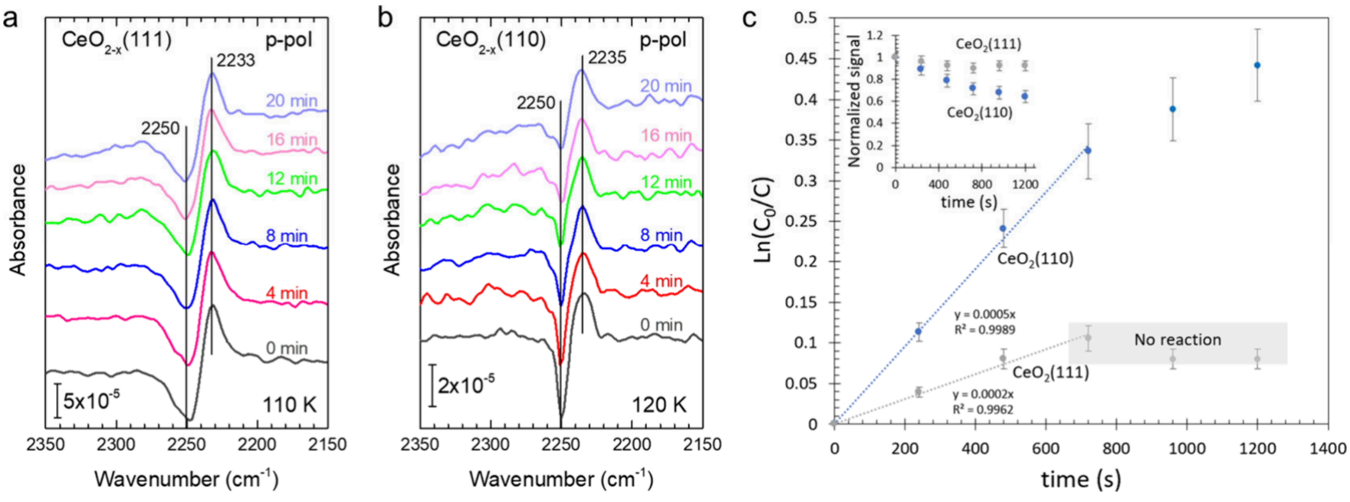

Figure 9. In situ IRRAS data of N_2O adsorbed on (a) reduced CeO_2(110) and (b) reduced CeO_2(111) surfaces as a function of UV irradiation (365 nm, 3.40 eV) time at 120 K. (c) Plot of $\ln(C_0/C_t)$ as a function of the UV irradiation time on both surfaces. Reproduced with permission from ref 63. Copyright 2022 American Chemical Society.

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combining different IR methods (polarization-resolved IRRAS, in situ IR transmission, is situ/operando DRIFTS) and using CO as a probe, profound insights into the surface structural evolution and chemical reactivity of ceria nanoparticles have been achieved, relying on the comprehensive and reliable reference data collected from ceria model systems.

This Account shows that probe-molecule infrared spectroscopy stands out as a powerful in situ/operando tool for studying the surface structure and surface chemistry of solid catalysts. However, more knowledge gained by the Surface Science approach is essential to establish robust benchmarks. Bridging the materials gap between model and real-world catalysts requires exploring more complex model systems, such as single metal atoms or clusters supported on ceria single crystals and other metal oxide systems. These systems can be fabricated with greater control compared to conventional wet chemical synthesis methods. While we have demonstrated the feasibility of probe molecule infrared spectroscopy working at the pressures up to 1 bar for powdered ceria systems, extending IRRAS measurements to single crystals under conditions approaching ambient pressure is essential to bridge the gap between surface science and practical catalysis research. It would be even more beneficial if the IRRAS measurements could be combined with kinetic measurements under realistic working conditions, which would significantly advance the understanding of heterogeneous catalysis at the molecular level. Importantly, results obtained from model catalysts can provide high-quality training data for artificial intelligence (AI) (algorithms - might be a more suitable word) used to analyze complex experimental IR spectra of real catalyst samples.

AUTHOR INFORMATION

Corresponding Author

Christof Wöll − *Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany;* orcid.org/0000-0003-1078-3304; Email: christof.woell@kit.edu

Authors

Chengwu Yang − *School of Energy and Power Engineering, Beihang University, Beijing 100191, China*
Hicham Idriss − *Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany;* orcid.org/0000-0001-8614-7019
Yuemin Wang − *Institute of Functional Interfaces, Karlsruhe Institute of Technology (KIT), 76021 Karlsruhe, Germany;* orcid.org/0000-0002-9963-5473

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.accounts.4c00529

Author Contributions

CRediT: **Chengwu Yang** conceptualization, data curation, supervision, validation, writing - original draft, writing - review & editing; **Hicham Idriss** writing - review & editing; **Yuemin Wang** writing - review & editing; **Christof Wöll** conceptualization, data curation, supervision, validation, writing - original draft, writing - review & editing.

Notes

The authors declare no competing financial interest.

Biographies

Chengwu Yang is an Associate Professor at the Beihang University (since 2018). He studied chemistry at the Karlsruhe Institute of Technology, where he received his PhD in 2016. He continued his postdoctoral research in the same group until he joined the faculty of Beihang University. His research interests lie in the field of surface science and industrial catalysis, particularly in the characterization of dynamic properties of model and actual catalysts.

Hicham Idriss received his BSc, MSc, PhD and Habilitation from the U. of Strasbourg (France). He started his academic career at the Department of Chemistry, U. of Auckland in New Zealand (1995−2008), then moved to the U. of Aberdeen and Robert Gordon U. (UK) to hold the Aberdeen Energy Futures Chair and Prof. of Chemistry position. He moved to corporate research at SABIC/KAUST (Saudi Arabia) in 2011. After retiring from SABIC in 2021, he moved to the Institute of Functional Interfaces at KIT (Germany) and is also a visiting scientist at the Joint Research Center of the European Commission (Karlsruhe). His main research area is in catalysis and surface reactions of oxides. He is also Professor (Hon.) at the Department of Chemistry, University College London, UK, since 2013.

Yuemin Wang is head of the research group "'Surface Catalysis"' at the Institute of Functional Interfaces (IFG) of the Karlsruhe Institute of Technology (since 2015). He studied Chemistry at the Nankai University and received his PhD in Physical Chemistry at the Fritz-Haber Institute of the Max-Planck Society in 2002. He joined the Ruhr-University of Bochum as a group leader in 2004. He served as Visiting Professor at the University of Technology Dalian (2008−2010) and Dalian Institute of Chemical Physics (2018−2019). His research interests are in the area of Surface Chemistry and Catalysis, especially vibrational spectroscopic studies on metal oxides and metal−organic frameworks.

Christof Wöll is Director of the Institute of Functional Interfaces (IFG) at the Karlsruhe Institute of Technology (since 2009). He studied Physics at the University of Göttingen and received his PhD in 1987 at the Max-Planck-Institute of Dynamics and Self-Organization. In 1996 he took over the chair for Physical Chemistry at the University of Bochum (until 2009) and founded the collaborative research center SFB 558. He has received several awards including the van't Hoff Prize of the German Bunsen Association. He is a member of the German National Academy of Sciences, Leopoldina and was the Spokesperson of the German Physical Society (DPG) Surface Physics Division (2016−2018). His research activities focus on fundamental processes in Surface Physics and Surface Chemistry, in particular development and advancement of techniques for the characterization of molecular adsorbates and oxide surfaces as well as metal−organic frameworks (MOFs and SURMOFs).

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