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Bridging the Pressure and Materials Gap in Heterogeneous Catalysis: A Combined UHV, In Situ, and Operando Study Using Infrared Spectroscopy

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ABSTRACT: The interactions of gas molecules with metal oxides used as catalysts or support materials in heterogeneous catalysis are highly intriguing. It is of great importance to gain detailed insight into the complex and often dynamic behavior of oxide particles under operando conditions. In this study, the understanding of CO interactions with cerium oxide surfaces is advanced by bridging the so-called materials and pressure gaps. This is accomplished by studying the influence of different types of materials, pressures, and temperatures by using different infrared spectroscopies as the primary investigation tool. Whereas low-temperature CO adsorption (<80 K) on various well-defined CeO_2 single crystal surfaces yields distinct vibrational bands that can be assigned to different adsorption sites on fully stoichiometric and also on reduced surfaces using validated ab initio calculations, strong gas-phase contributions turn the interpretation of results obtained for powders under operando conditions into a major challenge. By using a combination of UHV-IRRAS, in situ transmission infrared spectroscopy, and operando DRIFTS measurements, the reference data obtained for single-crystal surfaces under UHV conditions could be used to assign the features observed in spectra obtained for powder materials. In the next step, the different CO vibrational bands were used to monitor surface structural changes occurring at elevated pressures and temperatures. An increase in the concentration of Ce^{3+} species as a result of CO-induced reduction could be directly demonstrated even at low (300 K) temperatures. Our results demonstrate important progress toward the noninvasive, nondestructive characterization of real catalysts under operando conditions.
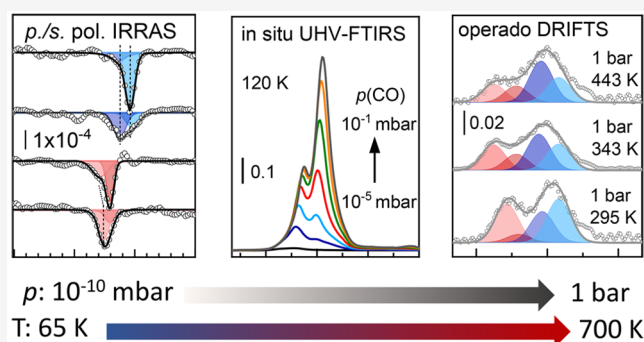
1. INTRODUCTION

Metal oxides play a major role in heterogeneous catalysis as active compounds as well as a support for metal particles. In order to elucidate the mechanisms of the often-complex reactions, it is of key importance to study chemical processes on the surface of oxide materials by combining powerful experimental techniques with theoretical work. The basis for understanding processes governing catalysis over oxide particles is provided by investigations on well-defined single-crystal surfaces studied under ultrahigh-vacuum (UHV) conditions. In a series of subsequent steps, the knowledge gained through the surface science approach for these model systems[1−5] allows for progression toward higher pressures, thus bridging the pressure gap. In addition, the insight, both experimentally and theoretically, gained for macroscopic single crystals has to be translated to describing chemical processes. This often occurs only on powdered nanoparticles present in technologically relevant catalysts, thus bridging the materials gap.

Research performed during recent years has shown that in a number of cases restructuring of catalysts occurs when the particles are exposed to reactive atmospheres at higher pressures, which cannot be observed under UHV conditions.[6−10] Because of the importance of closing the pressure gap, a number of advanced techniques have been developed aiming to allow for studies at elevated pressures, including IR, ESR, TEM, X-ray scattering, and X-ray absorption.[11] Among them, IR spectroscopy is one of the best suited techniques to study chemical processes occurring at the surface of heterogeneous catalysts in a wide range of pressures.[5,12−17] In particular, this technique can be applied to both well-defined model systems and nanostructured powders. However, IRRAS studies on macroscopic oxide single crystals are severely hampered by the inherent experimental difficulties due to the low reflectivity of the dielectric substrates. More

recently, the technical problems have been solved in connection with introducing surface ligand infrared spectroscopy (SLIR).[12] In the past years, an increasing number of well-defined model systems for understanding CO adsorbed on oxides have been established.[5,12,17–24]

One of the main problems in applying in situ/operando IR spectroscopy is the fact that both reactants and products occur in high concentrations in the gas phase. Rovibrational excitations related to these species dominate the spectra recorded at elevated pressures, thus making a reliable detection of adsorbates on the surface of the oxide particles a very challenging task.[25] In a number of previous works describing the application of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) to oxide powders in atmospheres of ambient pressure containing CO, IR bands have been assigned to vibrations of adsorbed CO. In many cases, these bands were located at around 2170 cm^{-1} and found to be rather broad, with FWHM (full width at half-maximum) values around 50 cm^{-1}. In the case of ceria, the topic of this paper, several authors have assigned this broad vibrational band at 2170 cm^{-1} to CO bound to uncoordinated Ce^{4+}. This assignment is somewhat surprising because in the corresponding data for CO adsorbed on ceria single-crystal surfaces and also on powder ceria materials vibrational peaks related to CO were found to have widths of about 10 cm^{-1} or less.[20–24]

In this context we would like to note that in spectra of gas-phase CO measured with a resolution of 4 cm^{-1} or larger, the individual rovibrational peaks (which are spaced by 3.6 cm^{-1}) are not resolved. In such cases, the R-branch of the gas-phase rovibrational spectra will appear as a broad wing centered around 2170 cm^{-1} with a FWHM width of about 50 cm^{-1} (see Figure 1). Of course, this broadening will depend on the gas temperature. We will come back to this point later.

In this work we have performed a systematic investigation on CO-induced surface structural changes of ceria particles at high pressures (up to 1 bar) using in situ/operando DRIFTS. Ceria (CeO$_2$) has in recent decades become one of the most important oxide materials in catalysis due to its unique redox property, which leads to the superior ability to store and release large amounts of oxygen.[26–30] We present a novel scheme that is based on recording high-resolution (2 cm^{-1}) spectra first for the reference gas phase and then for the powders. This approach allows us to unambiguously identify and then remove the CO gas-phase contribution from the operando DRIFTS data via a normalization/subtraction procedure in a reproducible fashion. The IR bands originating from CO vibrations on surfaces of ceria powders were clearly identified in these difference IR spectra. Importantly, these bands were found to have small widths of around 10 cm^{-1}, values much lower than the width of the R and P rovibrational branches observed for gas-phase CO. A detailed and conclusive assignment of CO vibrational bands was achieved based on reliable reference data reported previously for well-characterized ceria single-crystal surfaces by polarization-resolved infrared reflectance absorption spectroscopy (IRRAS) under UHV conditions.[20–24] The results obtained by combining DRIFTS, UHV-FTIRS, and UHV-IRRAS not only provide detailed information about CO adsorption sites on different facets but also reveal the CO-induced reduction of ceria nanoparticles under in situ and operando conditions for pressures up to 1 bar. Furthermore, the surface reduction and the formation of oxygen vacancies were further supported by observing an electronic transition between the f-states of Ce^{3+}
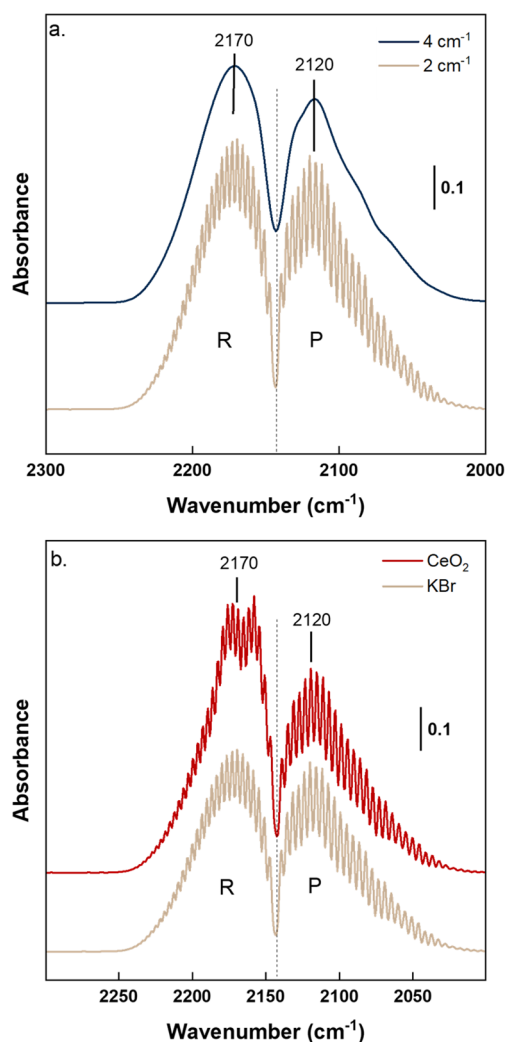

Figure 1. Raw DRIFTS data recorded for CeO$_2$ nanoparticles at a CO pressure of 1 bar at 295 K with a resolution of 4 cm^{-1} (a, black) and 2 cm^{-1} (b, red). For comparison, the reference spectrum for KBr powders (brown) in a CO pressure of 1 bar at 295 K is shown in (a) and (b).

ions, which gives rise to an IR absorption band at around 2120 cm^{-1}.[22,31–34]

2. EXPERIMENTAL SECTION

2.1. Ultrahigh-Vacuum Fourier Transformation Infrared Spectroscopy. The ultrahigh-vacuum Fourier transformation infrared spectroscopy (UHV-FTIRS) experiments were conducted with a sophisticated UHV apparatus combining a state-of-the-art FTIR spectrometer (Bruker Vertex 80v) and a multichambered UHV system (Prevac). This dedicated apparatus allows performing both IR transmission experiments on nanostructured powders and polarization-resolved IRRAS measurements on well-defined model catalysts (single crystals and supported thin films).[5,35]

The CeO$_2$ powder samples were calcined at 700 K in an Nabertherm B180 oven in static air for 12 h. Afterward, the sample (approximately 200 mg) was pressed into a stainless-steel mesh (150 × 150 wires/in., 0.37 open area, plain weave, Merck) and then mounted on a sample holder specially designed for transmission FTIR measurements. In order to remove unwanted surface contaminations like hydroxyl and

carbonate species, the sample was introduced into a preparation chamber (base pressure 1.3×10^{-10} mbar) and heated to 700 K for 30 min. Exposure to carbon monoxide (CO) was performed by using a leak-valve-based directional doser connected to a tube of 2 mm in diameter, which is terminated 3 cm from the sample surface and 50 cm from the hot-cathode ionization gauge. During the exposure, the sample temperature amounted to 120 K.

2.2. Operando DRIFTS. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measurements were performed in a VERTEX 80 Fourier transform infrared spectrometer (Bruker) equipped with Praying Mantis diffuse reflection optics (Harrick) and a liquid-nitrogen-cooled mercury cadmium telluride detector (LN-MCT). For the DRIFTS measurements, the powder sample was placed in a high-temperature in situ cell (Harrick) covered with a ZnS_2 window. The powder temperature is controlled by a heating cartridge below the cell and by a water circulation system. A strong temperature gradient exists in the DRIFTS cell[36] when comparing a sample in contact with the cell walls and in the center of the sample. For a proper interpretation, a correlation between the temperature set point and an actual temperature was calibrated prior to the experiments with an ImageIR 8300 camera (InfraTec) by monitoring the temperature on the surface of catalyst bed (used calibrations: M1x(30−150) and M1x(175−400) for temperatures between 295 and 1000 K. The temperature specification in the paper is based on the values observed with the ImageIR 8300 camera.

Prior to the CO absorption experiments, the powders were pretreated at 700 K for 2 h in 20% O_2/Ar. Afterward, the cell was cooled to the desired temperature where a background spectrum was recorded in O_2/Ar with a flow of 200 mL/min. Subsequently, the DRIFTS experiments were performed in pure CO at the dedicated pressures and temperatures.

2.3. Normalization/Subtraction Scheme. A crucial step in this work was developing a scheme for removing the rovibrational peaks originating from gas-phase CO. A simple computation of difference spectra from normalized spectra, as typically used in DRIFTS applied to samples in a CO atmosphere, was found to be insufficient. Instead, we used a procedure where the KBr reference and the ceria powder data were first normalized in a narrow frequency window between 2080 and 2040 cm^{-1}. The choice of this interval is motivated by the fact that in this regime no CO surface vibrational bands are present. Also, the electronic transition at about 2120 cm^{-1} is located outside this frequency window. Subsequently, the KBr data were subtracted from the ceria data. In the resulting spectra (see Figure 2) the rovibrational bands were so strongly reduced in intensity that a fitting routing using the known positions of the CO vibrational bands on stoichiometric and reduced ceria substrates can be applied (see Figure 2).

3. RESULTS AND DISCUSSION

Prior to the operando DRIFTS measurements, the CeO_2 powder samples were cleaned by heating in oxygen at 720 K for 2 h in order to remove all surface contaminations, such as carbonate and hydroxyl species. They are known to give rise to numerous vibrational bands, which obscure the signals from adsorbed CO. In addition, these contaminations block adsorption sites, so that the uptake of CO is reduced. As shown in Figure S1, only very weak OH and carbonate/formate-related IR bands are observed after the cleaning
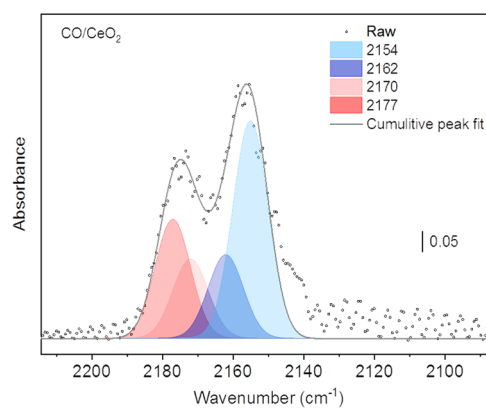

Figure 2. Deconvoluted difference DRIFT spectrum (dotted line) of CO adsorbed on CeO_2 nanoparticles recorded at a CO pressure of 1 bar at 295 K, after normalization and application of the normalization/subtraction procedure (see text).

treatment, revealing that surface contaminations have been largely removed.

Figure 1a displays the raw DRIFTS data recorded for CeO_2 powders exposed to CO at ambient pressure (1 bar) immediately after the cleaning procedure. The spectrum with a resolution of 4 cm^{-1} is dominated by two broad IR bands centered at about 2170 (R-branch) and 2120 cm^{-1} (P-branch) with a FWHM value of about 50 cm^{-1} originating from gaseous CO. The high-resolution (2 cm^{-1}) DRIFT spectrum shows rovibrational fine structure CO bands in the gas phase derived from the ν_1 CO stretching vibration at 2143 cm^{-1}. More than 55 of these bands spaced by 3.6 cm^{-1} are visible. Although we know from the corresponding UHV studies that under these conditions CO species adsorbed at the surface of ceria nanoparticles must be present, in the raw data these adsorbate vibrations are almost completely obscured by the intense gas-phase signals. The situation is improved by recording reference spectra for KBr powders[37] (Figure 1b), a material where under these conditions (295 K, 1 bar CO) the amount of CO adsorbed on the surface is negligibly small.[38]

We find that in the difference spectra obtained by first normalizing the spectra in the frequency regime between 2080 and 2040 cm^{-1} and then subtracting the KBr reference data from the ceria data, vibrational bands arising from CO adsorbed on ceria surfaces can be clearly identified (Figure 2). After the subtraction scheme, the difference DRIFT spectrum clearly shows two peaks centered at 2157 and 2175 cm^{-1} with a FWHM value of around 13 cm^{-1}. It therefore appears that the width of the features seen in the gas-phase spectra can serve as a unique criterion as to whether a feature is assigned to gas-phase signals or to adsorbate-related vibrational bands. While the value of about 13 cm^{-1} reported here is approximately a factor of 2 larger than the signals seen for CO adsorbed on ceria single crystals and about 50% larger than the signals seen for CeO_2 powder particles, the width is clearly smaller than that (around 50 cm^{-1}) of the broad IR signals observed previously for CO on ceria.

We have a closer inspection of the CO-related DRIFTS data by quantitative fitting. Figure 2 shows the deconvoluted spectrum in which four IR bands are resolved at 2154, 2162, 2170, and 2177 cm^{-1}. An additional weak shoulder is also visible at around 2120 cm^{-1}. Based on the reliable reference data acquired using polarization-resolved IRRAS for oxidized and reduced ceria single crystals on all three low-index (111),

(110), and (100) surfaces investigated recently in our group and recent state-of-the-art computational results,[20−24,39] the dominating IR band at 2154 cm^{-1} is characteristic for CO adsorbed at surface Ce^{4+} sites exposed by oxidized CeO_2(111) facets while the 2162 cm^{-1} band is attributed to CO bound to the reduced CeO_2(111) surface in the presence of Ce^{3+} ions and surface/subsurface O vacancies. The two high-lying IR vibrations at 2170 and 2177 cm^{-1} are assigned to CO species adsorbed on the oxidized (Ce^{4+} sites) and reduced (Ce^{3+} sites) CeO_2(110) facets, respectively.

On the basis of our DRIFTS data in Figure 2, we can state that the surface vibrational bands for CO bound to ceria substrates—even if measured at ambient pressure—have a FWHM smaller than 10 cm^{-1}. In our measurements performed with a resolution of 2 cm^{-1} we can clearly resolve the CO-related vibrational bands, and no broad bands with a FWHM value on the order of 50 cm^{-1} were observed.

To the best of our knowledge, this is the first case in which individual adsorbate peaks could be resolved in DRIFTS data recorded for ceria at CO pressures up to 1 bar and then assigned in a one-to-one fashion to CO adsorbates on the different facets of ceria including both Ce^{4+} and reduced Ce^{3+} sites.

For a better understanding of CO adsorption on ceria over a vast pressure and temperature range, the ceria powder sample was subsequently introduced into an UHV apparatus dedicated to UHV-FTIRS study of metal oxides.[12,35] Here the CeO_2 nanoparticles were investigated at low temperatures (120 K) and down to UHV conditions. The in situ UHV-FTIRS results are listed in Figure 3. The low-pressure (10^{-5} mbar) CO
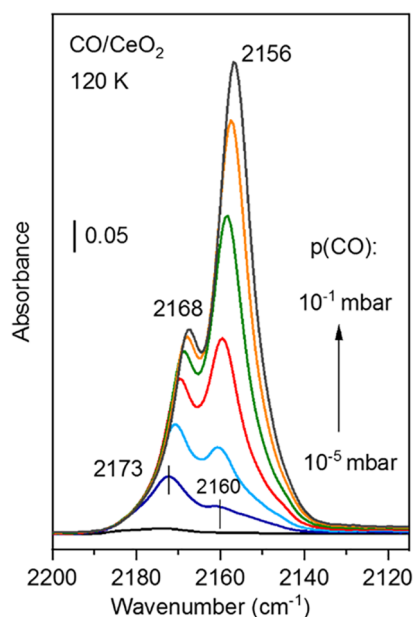
Figure 3. In situ UHV-FTIRS data recorded for CeO_2 nanoparticles exposed to CO at 120 K with a low pressure increasing from 10^{-5} to 10^{-1} mbar.

adsorption on ceria powders at 120 K leads to the appearance of two bands around 2173 and 2160 cm^{-1}, which are respectively attributed to CO bound to reduced ceria (110) and (111) facets with higher binding energies than those of CO on oxidized ceria surfaces.[20−24] By increasing CO pressure up to 1×10^{-1} mbar at 120 K, CO adsorbed at Ce^{4+} sites on

oxidized ceria (111) and (110) facets becomes majority species, as evidenced by the frequency shift of dominating CO vibrational frequencies to 2156 cm^{-1} (CO−CeO_2(111)) and 2168 cm^{-1} (CO−CeO_2(110)).[20,21]

In order to demonstrate the potential of such DRIFTS studies at elevated pressures for operando studies, in a next step, we investigated the CO-induced structural changes of ceria nanoparticles at ambient pressure as a function of temperature. The corresponding deconvoluted DRIFT spectra obtained after applying the normalization/subtraction procedure described above are presented in Figure 4. For
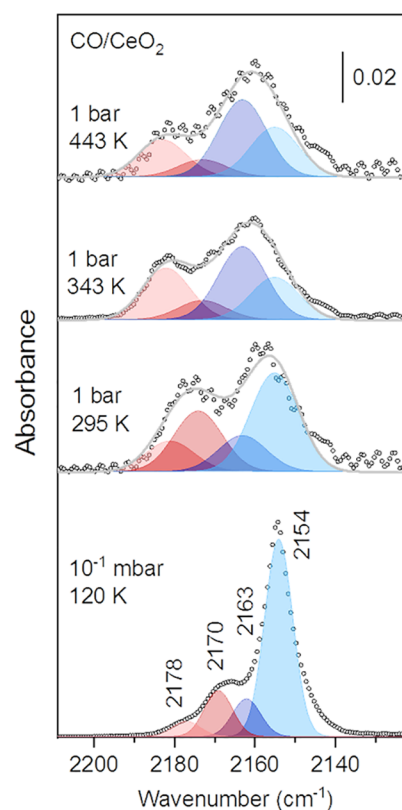
Figure 4. Deconvoluted difference DRIFTS data of CO adsorbed on CeO_2 nanoparticles recorded in a CO pressure of 1 bar at different temperatures (295, 343, and 443 K), obtained after normalization and application of the normalization/subtraction procedure (see text). For comparison, the in situ UHV-FTIR spectrum recorded for CeO_2 in 1 × 10^{-1} mbar of CO at 120 K is also shown.

comparison, the UHV-FTIRS data for CO adsorption at lower pressure (10^{-1} mbar) and lower temperature (120 K) are also shown. Whereas in the latter case the ceria nanoparticles expose predominantly oxidized (111) facets showing the characteristic CO band at 2154 cm^{-1} as the most intense peak, we clearly observed a significant increase in intensity of the vibrational band at 2163 cm^{-1} with increasing the CO pressure and sample temperature. This IR signal becomes the main CO band in the DRIFT spectrum recorded in 1 bar of CO at 443 K. As discussed above, the 2163 cm^{-1} band is assigned to CO bound to reduced CeO_2(111) facets.[20−24] These IR results provide direct spectroscopic evidence for the CO-induced reduction of the ceria surfaces at elevated pressures and temperatures.

In addition, a broad signal at 2120 cm^{-1} shows up when subjecting ceria nanoparticles to CO (1 bar) at 443 K. In

contrast to the aforementioned CO adsorbate vibrations, which are all blue-shifted relative to gas-phase CO (2143 cm^{-1}), the IR feature at 2120 cm^{-1} exhibits a red-shift. Based on our systematic IRRAS investigations on all three low-index ceria single-crystal surfaces in both oxidized and reduced states, a red-shifted IR band cannot be assigned to an adsorbed CO species.[20−24] Indeed, it has been reported that this IR absorption band is not attributed to an adsorbate vibrational excitation but to an electronic transition ($2F_{5/2} \rightarrow 2F_{7/2}$) related to the presence of reduced Ce^{3+} cations.[22,31−34] Therefore, the IR signal at 2120 cm^{-1} provides additional independent proof of the surface being reduced in the presence of CO at ambient pressure.

After exposure of CO to the ceria surface, reduction readily occurs, even at a low temperature. In Figure 5 we evaluate this
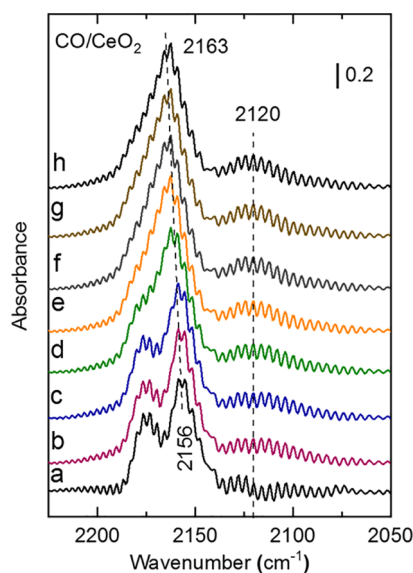

Figure 5. Spectral evolution of difference DRIFTS data of CO adsorbed on CeO$_2$ nanoparticles recorded in a CO pressure of 1 bar at 295 K as a function of time: (a) 2, (b) 3, (c) 4, (d) 5, (e) 10, (f) 20, (g) 30, and (h) 45 min.

CO-induced structural evolution of CeO$_2$ nanoparticles at room temperature, based on the spectral evolution of the difference DRIFTS data at a constant CO pressure of 1 bar as a function of time. After introducing CO into the reaction chamber, a predominant band appears at 2156 cm^{-1} resulting from CO adsorbed at Ce^{4+} sites on oxidized CeO$_2$(111) as the majority facets exposed by ceria nanoparticles. Exposure to CO at 295 K for 45 min leads to a blue-shift of the main peak from 2156 to 2163 cm^{-1} being characteristic for CO on reduced ceria (111) surfaces, Furthermore, the Ce^{3+}-related electronic excitation at 2120 cm^{-1} starts to increase in intensity with prolonged exposure to 1 bar of CO at 295 K and reaches a maximum after 30 min (Figure 5). Overall, these findings reveal a substantial increase in the amount of oxygen vacancies, demonstrating the onset of CO-induced surface reduction of ceria nanoparticles already at room temperature.

4. CONCLUSIONS

In summary, the combination of complementary IR methods applied at different pressures and temperatures allowed for new insights into the CO-induced structural changes of ceria particles under operando conditions. Because the vibrational

bands of the adsorbed CO are hidden underneath the gas-phase rovibrational bands, a novel normalization/subtraction scheme was developed to remove the gaseous CO signals. This data processing allowed, for the first time, reproducible and reliable detection of various CO surface vibrational bands under ambient conditions. We thus challenge previous works (see above) and assign the broad (FWHM values of 50 cm^{-1}) IR band located at about 2170 cm^{-1} to the R-branch of gas-phase CO.

These studies, bridging not only the pressure but also the materials gap, allowed us to investigate the interaction of ceria powders with carbon monoxide, in particular the CO-induced reduction of ceria particles, in a straightforward and reproducible fashion within a wide pressure and temperature range. Using the comprehensive IRRAS data acquired in our group on well-defined ceria single crystals as a reference database, four well-recognizable adsorption bands at 2177, 2170, 2162, and 2154 cm^{-1} were identified and assigned to the different ceria facets and the oxidized as well as reduced surfaces. No new bands were detected for the powder particles; all observed features could be assigned on the basis of the (macroscopic) single crystal data for ceria (110) and (111) surfaces. Additionally, a broad band around 2120 cm^{-1} which corresponds to the electronic transition of reduced Ce^{3+} cations was also resolved below the gas-phase signal, which is proof for the existence of reduced ceria in the CO atmosphere, even at low (300 K) temperatures. Our study shows that by combining different infrared spectroscopy techniques, which are suited for a broad range of temperatures and pressures, as well as using small molecules, such as CO as surface ligands, a detailed and sophisticated analysis of metal oxides is possible, and the pressure and materials gap can be bridged.

This conclusion is essential for further investigations regarding metal oxide particles or even catalysts, composed of noble metals on top of metal oxides, where an operando investigation at higher temperatures and higher pressures, especially for CO oxidation, is of utmost importance. This method, in combination with the gas-phase removal, could be used in industry applications or under operando conditions without the use of UHV equipment, which is for such cases highly unpractical and not feasible.

■ ASSOCIATED CONTENT

ⓈI Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c03567.

Additional results obtained from DRIFTS investigations (PDF)

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Notes

The authors declare no competing financial interest.

Biographies

Lachlan Caulfield received his Master's degree in the Department of Chemistry from the University of St. Andrews, and he is currently a Ph.D. candidate in the group of Prof. Christof Wöll at the Karlsruhe Institute of Technology. He has been working in the field of the characterization of metals and metal oxides with in situ and operando IR spectroscopy to track active sites on catalytic surfaces.

Eric Sauter received his Ph.D. degree from the Ruprecht-Karls-University Heidelberg, under the supervision of Professor Michael Zharnikov. He is currently a Research Scientist in the Group of Professor Christof Wöll and joined the Institute of Functional Interfaces, Department of Organic and Oxidic Interfaces, at the Karlsruhe Institute of Technology. His current research interests focus on the characterization of metals and metal oxides with in situ and operando IR spectroscopy for a better understanding and optimization of heterogeneous 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), and 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 of the Karlsruhe Institute of Technology since 2014. He received his PhD at the Fritz-Haber Institute of the Max Planck Society with Prof. Gerhard Ertl and Prof. Karl Jacobi in 2002. He joined the Ruhr-University Bochum as group leader in 2004 and served as a visiting professor at the University of Technology Dalian (2008−2010). His research interests are fundamental processes in surface chemistry and catalysis, focusing on vibrational spectroscopic studies of metal oxides and metal−organic frameworks (MOFs).

Christof Wöll is the director of the Institute of Functional Interfaces at the Karlsruhe Institute of Technology since 2009. After his studies of physics at the University of Göttingen he received his PhD in 1987 from the Max-Planck-Institute of Dynamics and Self-Organization in Göttingen. After a postdoctoral time (1988−1989) at the IBM research laboratories, San Jose, CA, he accepted a position equivalent to Assistant Professor at the Institute of Applied Physical Chemistry, University of Heidelberg. After his habilitation he took over the chair for Physical Chemistry at the University of Bochum (until 2009). His research interests focus on fundamental processes in surface physics and surface chemistry, development and advancement of techniques for the characterization of molecular adsorbates and oxide surfaces, organic surfaces, and metal−organic frameworks (MOFs). He has been a member of the German National Academy of Sciences, Leopoldina, since 2016.

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