A high-temperature, ambient-pressure ultra-dry operando reactor cell for FT-IR Spectroscopy

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Abstract

The construction of a newly designed high-temperature, high-pressure FT-IR reaction cell for ultra-dry in-situ and operando operation is reported. The reaction cell itself as well as the sample holder is fully made of quartz glass, with no hot metal or ceramic parts in the vicinity of the high-temperature zone. Special emphasis was put on chemically absolute water-free and inert experimental conditions, which includes reaction cell and gas-feeding lines. Operation and spectroscopy up to 1273 K is possible, as well as pressures up to ambient conditions. The reaction cell exhibits a very easy and variable construction and can be adjusted to any available FT-IR spectrometer. Its particular strength lies in its possibility to access and study samples under very demanding experimental conditions. This includes studies at very high temperatures, e.g. for solid-oxide fuel cell research or studies where the water content of the reaction mixtures must be exactly adjusted. The latter includes all adsorption studies on oxide surfaces, where the hydroxylation degree is of paramount importance. The capability of the reaction cell will be demonstrated for two selected examples where information and in due course a correlation to other methods can only be achieved using the presented setup.
I. Introduction

Infrared Spectroscopy is one of the most effective spectroscopic methods to characterize surface reactions of heterogeneous catalysts\(^1\). One of its great strengths thereby is the possibility to also operate at ambient conditions\(^2\). Hence, in fundamental research this method is already a widely used specific tool to visualize not only the interaction between gas phase and solid, but also to identify certain surface-related properties during chemical or catalytic reactions\(^3\). Thus, in the particular case of studying reaction mechanisms an in-situ or, better still, an operando setup is mandatory\(^4\). However, the effective limitations of FT-IR spectroscopy are easily approached e.g. upon dealing with SOFC (solid oxide fuel cell) related research. Here, certain challenges must be dealt with, as typically high pressures and high temperatures in the range of ambient pressure and temperatures up to 1273 K are usually necessary\(^5\). SOFC-relevant heterogeneous catalytic research is mainly based on metal-oxide-composites such as the well-known anode material Ni-YSZ (nickel in combination with yttria-stabilized zirconia with mostly 8mol\% yttrium), which is already used in industrial processes\(^6\). Increasingly, the focus in fundamental research also lies on the characterization of pure oxides without metal parts, whereby apart from simple structural aspects, the level of hydroxylation and the amount of defects is a crucial factor steering the reactivity towards catalytic interaction with gaseous reactants\(^7\). Infrared methods have been proven to be a particularly useful tool in both qualitative characterization and in quantifying such surface-related aspects\(^1\). Revisiting the related functional requirements of an operating SOFC, a quite sophisticated system, exceeding the use of simple in-situ reactor cells, is needed to control especially the amount of humidity. As it will be shown in the present contribution, this has turned out be quite complex due to the desired operando measuring mode. With respect to YSZ and its ‘oxide building blocks’, the hydroxylation degree has been revealed to be of
particular importance for adsorption and reduction processes. The formation and following

temperature-controlled reaction of carbon dioxide with the oxide surface is a good indicator of

the amount of hydroxylation due to the formation of (bi-)carbonates and furthermore will be

used to monitor the dehydroxylation and drying efficiency of the new set-up.

Another limitation of conventional FT-IR operation is approached upon discussion of the

interaction of methane with the oxide surfaces at operating temperatures of the SOFC. Our

previous investigations on yttria, zirconia and YSZ proved that the pure oxides may act as

efficient mediator steering the methane-induced carbon deposition and the formation and/or

growth of different carbon species at temperatures between 1073 K and 1173 K. In due

course, a spectroscopic study is needed to shed additional light on the reaction mechanism of

methane decomposition and the spectroscopic investigation of possibly associated reaction

intermediates. For this, however, very high temperatures of at least 1100 K are necessary,

which is out of range of conventional in-situ FT-IR reactor cells.

Throughout the last 60 decades, the construction of a suitable reaction cell for such extreme

purposes has been a crucial topic, both for many research groups but also IR-device

manufacturers. Up to now, there are several in-situ transmission cells for the above mentioned

applications (gas-solid-system) available on the market and self-built setups reported, respectively. Nevertheless, most of them suffer severe drawbacks: usually metallic

and/or ceramic components are present in the heated reactor part as a consequence of

facilitated engineering. Unfortunately, those materials can have a significant influence on the

desired reactions, even multiplied by the required extreme pressure and temperature

conditions. Among those, especially stainless steel and carbon monoxide is an unfortunate

combination, because carbon monoxide is able to form Ni-carbonyl species, which is of

course highly disadvantageous. However, the large majority of cell models in literature still

comprise steel parts in the heated region. In due course, the potentially more problematic elements inside some reported reaction cells are inner heating coils.
thermo element wires composed of metal components such as Ni, Cr, Pt and Rh\cite{19, 27, 31} or even sample holders containing certain ceramics or metals\cite{2, 21, 28, 31}. Ambient or higher pressure systems are not a great challenge with respect to technical construction, whereas concerning accessible temperature range, only very few in-situ cells allow a sample treatment above 873 K such as described in references\cite{30, 34}. In the case of Pomfret et. al.\cite{34, 35} the described cell is a highly specialized fuel cell reactor with operating electrodes inside the in-situ cell for FTIR emission measurements. One of the very few transmission cells with a completely inert sample environment was constructed by Weag et al.\cite{30} with an inner quartz tube and outer heating and thermo element to provide an inert sample area - its highest operation temperature is, however, limited to 973 K.

In order to meet these demanding criteria, a specific reaction cell with at the same time an absolutely inert and water-free sample environment and the possibility to perform in-situ and operando spectroscopy at ambient pressures and very high reaction temperatures has been constructed and tested in CO$_2$ adsorption and methane decomposition on Y$_2$O$_3$. Following this approach, the reactor cell is entirely constructed from quartz glass, which is combined with efficient gas pre-treatment regarding humidity in the admitted gases.

The result of our efforts is a high-temperature, ambient pressure reactor cell for FT-IR spectroscopy in operando transmission mode combined with a highly flexible gas supply for specific applications. Except for the enhancements concerning physico-chemical advantages, this cell also provides a very simple and quite variable construction and therefore can be attached to most of the commonly used and commercially available transmission IR-spectrometers. A particular advantage is the high flexibility of all components: IR windows, flange size, height and size of the quartz tube are easily adjustable to special needs.
II. Experimental Setup

A. Construction and technical design

Figure 1
Scaled schematic 3D drawing of the in-situ/operando IR cell. (A) CF flange for gas supply, (B) multi-purpose side flange, (C) IR-window holder, (D) IR-window, (E) Viton seal, (F) water cooling lines, (G) Ni/NiCr thermo element, (H) heating wire, (I) ceramic heat shield, (J) threaded rod, (K) sample disc, (L) quartz sample holder, (M) quartz tube, (N) cooled copper shield.
This reactor cell (Figure 1) consists of a quartz tube (M) mounted between two specially designed steel flanges (B). These flanges provide the gas in-/outlet (A), an effective water cooling system (F, N) and the IR transparent windows (D). For coupling of the special side flanges and the quartz part, the tube is placed between these metal units pressed against Viton seals in order to seal the cell via three threaded rods (J), linking the two flanges together. The pressed powder pellet sample (10 mm diameter, ~0.1 mm thickness, 50 mg sample mass) (K) is placed inside in the center of the quartz tube (M, 19.5x2.7x158 mm) equipped with a specially designed quartz sample holder (L, 12x2x38 mm tube with a 2 mm slot in the center). The basic idea was to construct the heated inner sample part exclusively from quartz. The functional side flanges are made by stainless steel (max. 70 mm outer diameter), which must be accordingly effectively cooled in order to eliminate every potentially reactive heated metal or ceramic component. This is achieved by a copper cooling shield (N) coupled directly to the water cooling of the side flange, which also covers about 20 mm on each side of the quartz tube. Even at a sample temperature of 1273 K the flange temperature does not get hotter than the cooling water temperature. The outer heating coil (H) is a resistive wire (d = 0.7 mm, 3.51 Ω m⁻¹, Kanthal) wrapped around the center of the quartz tube in 24 windings over a range of 50 mm (total length of about 1.7 m, total resistance = 6 Ω). The part of the heating wire that penetrates the ceramic heat shield (I, alumina based, 35x5x60 mm) is twisted with a reverse heating wire in order to suppress additional heat generation and is also covered with a ceramic tube (3 mm outer diameter) before it is contacted via a ceramic plug to the power supply and controlling unit. The outer thermo element (G) (Ni/NiCr, d = 0.2 mm) is also covered with a ceramic tube (1.5 mm outer diameter) on its full length and is placed underneath the tightly coiled heating wire. The contact point of the Ni and NiCr wires is located exactly in the center of the cell where the sample is placed. Nevertheless, a calibration of the inner temperature at this point must be accurately performed over the whole temperature range up to 1273 K (see section “Functionality, parameterization and purity”). The thermo element is also connected
to the controlling unit via a ceramic plug/coupler with heat-resistant connecting cables. The infrared transparent windows (D) are easily interchangeable and can be different window materials e.g. CaF$_2$ or BaF$_2$ (both supplied by Korth Kristalle GmbH) can be used. In general, the windows have a thickness of 2 mm and a diameter of 20 mm. They are placed between 2 Viton O-rings and are positioned using a stainless steel ring (C), whose inner diameter defines the maximum inlet of the beam path of 14 mm.

On the whole this in-situ cell has a full length of 198 mm, but it is constructed in a way that a certain flexibility in the length of the quartz tube is obtained and consequently, the cell can be adjusted to the typically used spectrometer gaps. The cell is held in position with the help of a simple metal framework that defines the height of the beam path, which can also be adapted to any spectrometer.

B. Functionality, parameterization and purity

As one of the most important features is the possible use at very high temperatures, the corresponding temperature control and calibration is of uttermost importance. Therefore the temperature at the exact position of the sample pellet inside the quartz tube was calibrated by an additional thermo element inside the quartz reactor cell over the whole accessible temperature range between room temperature and 1273 K before final mounting of the sample. For this purpose, both temperatures were compared every 20 K step and the eventual deviation used to calibrate the temperature reading. Due to the fact that an unshielded two-point control of the heat regulation can disturb the collection of the infrared spectra a controller with an analogue output for a dc-current controlled power is used (JUMO cTRON 04/08/16). To reach a temperature of 1273 K, a current of about 6.5 A has to be applied (provided by a Digital Labornetzgerät PS 3065-10B 650W EA Elektro-Automatik). Below 973 K the temperature deviation is around 5 K but the deviation increases up to 20 K at the
highest temperature. In any case, accurate temperature calibration is possible. At this point, the problems with collecting IR spectra at very high temperatures should be very briefly discussed. At these temperatures, in principle materials will emit IR radiation, in consequence disturbing the measurements. In due course, there are hardly any IR spectra reported in literature collected above 873 K, simply because the overwhelming majority of the used cells do not operate in this temperature range. Nevertheless, the intensity of the background radiation caused by heat impact has its maximum influence at 873 K and above this temperature (and up to 1273 K) no further baseline shift or any other influence of the heat radiation is observed.

The pressure of the cell (reactor volume ~ 110 ml) is measured using a Pirani gauge (TPR 010, BALZERS) positioned directly above the CF-flange of the cell. High-Vacuum is obtained by a HiCube 80 Eco turbo molecular pumping station (PFEIFFER) resulting in base pressures of 5x10⁻⁷ mbar in the cell and 5x10⁻⁶ mbar in the whole apparatus including gas feeding lines (controlled by an IKR 050 cold cathode ionization gauge, BALZERS).

The setup can be operated both under flowing and static conditions. In general, the gas feeding line is made from copper exclusively. This is especially important when reactive gases like CO are used, which e.g. could form carbonyl species with stainless steel components for longer expositions. As this would interfere with measuring reaction rates, this is, of course, highly undesirable especially under operando conditions relevant for catalysis.

As a standard procedure, all used gases and gas mixtures are cleaned by liquid nitrogen/LN₂-ethanol cooling traps. To obtain extremely dry static conditions pre-adsorption of the gases on an additionally installed Zeolite trap (5Å) and subsequent release of the gases into the reactor cell must be performed. In contrast, deliberate admission of moisture and to subsequently perform experiments with water-saturated gases in flowing or static mode is possible upon use of a home-built water vapor saturator.
With this set-up reproducibility also applies to the sample pretreatment. Since the parameters temperature, pressure, gas flow, gas composition and especially moisture can be exactly varied, the starting conditions for any experiments can be exactly defined by the pre-treatment.

Another important technical aspect is the necessary stability and reproducibility of the background. To ensure almost identical background conditions the spectrometer itself as well as the detector and the small slots between cell and spectrometer are purged with gaseous nitrogen.

We emphasize already at this stage, that only under the rather demanding drying procedures in combination with the described gas feeding line setup, the influence of moisture and hydroxylation can be exactly studied, which is a prerequisite for studies on oxide surfaces. This will be highlighted in section III in selected examples.

III. Applications

All spectra shown in section III were performed with a Perkin Elmer Spectrum 2000 FT-IR Spectrometer. The following experiments were chosen to explicitly demonstrate the particular advantages of this setup. The special reaction parameters are given in the respective Figure captions. More details about the experimental conditions of Electrochemical Impedance Spectroscopy, Volumetric Adsorption and special sample pretreatments are discussed in references\textsuperscript{8, 9}. It will be shown in both cases how additional crucial information can be obtained by FT-IR spectroscopic experiments under the very demanding conditions of ultra-high purity and high temperatures.

A. Adsorption of CO\textsubscript{2} on Y\textsubscript{2}O\textsubscript{3}
The highlighted spectra in Figure 2 A and B are extended investigations of the previous experiments of carbon dioxide adsorption on yttria published recently\(^8\) (for comparison, see supplementary material (Figure S1 panels A and B) for FT-IR spectra following CO\(_2\) adsorption with the previous setup\(^36\) or Figure 1 and 3 in ref.\(^8\)). At this point, the specific improvements to the previous setup in ref.\(^8\) should be mentioned: in essence, the former steel reactor cell has been replaced by a reaction cell fully made of quartz glass to access the required high temperature regime and both the heating coils and the thermocouple are mounted outside the reactor cell itself to remove any reactive material from the high-temperature zone. In addition to the improvements regarding the purity of the gas-feeding lines and the cell itself, this allows the ultra-dry operation at high temperatures, as outlined. As already emphasized in that former publication, the crucial factor determining the adsorption properties is the hydroxylation of the sample. For an extremely hygroscopic oxide sample (as Y\(_2\)O\(_3\)) every single trace of water possibly adsorbs on the surface, subsequently steering the distribution and nature of the resulting adsorbates. Especially for Y\(_2\)O\(_3\), which is extremely sensitive against CO\(_2\) even at room temperature, we expect strong differences in the absolute amount and distribution and possibly also in the nature of the subsequently adsorbed carbonates. Consequently, this experiment is perfect for testing the set-up for moisture-sensitive requirements.
Figure 2

In-situ collected FT-IR spectra following static adsorption of CO$_2$ on pure Y$_2$O$_3$ at room temperature and pressures from 8x10$^{-6}$ mbar up to 10 mbar taken with the setup described in here. Panel A shows both the OH- and the carbonate-region; panel B an expanded view of the distribution of the different carbonates.

The static adsorption of CO$_2$ on oxide surfaces at room temperature leads to formation of (bi-)carbonates on the surface via insertion of the CO$_2$ molecule into surface OH-groups\textsuperscript{37}. The distribution and total amount of the different kinds of (bi-)carbonates is dependent on the major variables temperature, pressure, sample pre-treatment and the resulting degree of hydroxylation. As temperature and pressure conditions have been chosen to exactly the same in both experiments (i.e. the previous and the present setup), only the remaining moisture in the cell and the directly related amount of surface hydroxylation is considered to crucially influence the nature and distribution of the resulting carbonate species. Upon comparison of panels A and B with those taken with the previous setup (cf. Figure S1 panels A and B, as well as Figures 1 and 3 of ref.\textsuperscript{8}) it is obvious that the gas phase signal of CO$_2$ is apparently larger in the present experiment. The only exception concerns the much drier conditions used in the present experiments – indicating suppressed adsorption of CO$_2$. This is in line with the fact that the chemisorption strongly depends on the hydroxylation degree of the surface. In close correlation, the intensity of the (bi-)carbonate species in the region below 1900 cm$^{-1}$ is about 6 times lower in the drier experiment compared to the previous set-up. This is also corroborated by the fact that there is no broad OH-signal below 3500 cm$^{-1}$ caused by interacting hydroxyl groups of the formed bicarbonates. The detailed assignment of the signals in the region of the $\nu_s$, $\nu_{as}$ and $\delta_{OH}$ vibrational modes in Panel B show that also the distribution of the different kinds of (bi-)carbonates is steered by the amount of OH-groups. In the former experiment under less dry conditions, i.e. with more hydroxyl species (see
supplementary material (Figure S1 panel B) for FT-IR spectra in the carbonate region following CO\(_2\) adsorption with the previous setup\(^{36}\), or Figure 3, ref. \(^8\)), the monodentate bicarbonate is the dominant species at pressures below 2 mbar and at 10 mbar the bidentate bicarbonate becomes the predominant feature. Nevertheless, the amount of the monodentate bidentate is still quite high. The previous experiment also shows a broader distribution of the different (bi-)carbonates (see supplementary material (Figure S1 panel B) for FT-IR spectra in the carbonate region following CO\(_2\) adsorption with the previous setup\(^{36}\) or Figure 3, ref. \(^8\)). However, in the drier experiment the bidentate carbonate is obviously by far the most common.

\textbf{B. Methane decomposition on } Y\(_2\)O\(_3\) \\

Methane dissociation leading to carbon deposition on yttria starts and proceeds at above 1000 K, which has previously been in detail studied with in-situ EIS (Electrochemical Impedance Spectroscopy) and in-situ Volumetric Adsorption techniques\(^9\). As the necessary temperatures are very high, the related requirements for the in-situ FT-IR experiment are consequently also temperatures up to 1173 K. Furthermore, for providing a directly related spectroscopic proof of possible reaction intermediates, the FT-IR experiments should be preferably done under exactly the same or at least comparable experimental conditions. Thus FT-IR spectra have to be collected under operando conditions, i.e. directly at very high temperatures. It is worth noting, that in principle reaction cells for pretreatments at high temperatures exist, but no direct transmission spectroscopy\(^{23}\), because the sample has to be re-cooled for spectra acquisition. One notable exception is the cell reported by Weng et. al. also allowing transmission spectroscopy at 973 K\(^{30}\). However, whereas the reactor cell itself is stated to be made from quartz glass, the material of the sample holder inside the cell is not mentioned. We also note that this particular transmission cell, which is the only one coming close to the
performance of our transmission cell, would nevertheless be insufficient for studying the
methane decomposition on this oxide. Our setup, however, allows overcoming these
restrictions, by performing spectroscopy directly at the required high temperatures. In due
course, the corresponding electric impedance and volumetric adsorption traces upon heating
and cooling can be exactly followed by IR-spectroscopy. Experiment-wise, in the case of EIS,
flowing conditions (methane flow = 0.7 ml s\(^{-1}\), pressure = 1 bar) and heating and cooling rates
of 10 K min\(^{-1}\) have to be applied. For the IR equivalent of the corresponding volumetric
adsorption experiment a static methane atmosphere of 90 mbar CH\(_4\) and similar heating and
cooling rates of 10 K min\(^{-1}\) were necessary.

Figure 3 shows the combination of the in-situ EIS measurement of heating and cooling in
methane with the directly related operando FT-IR spectra collected at selected temperatures.
The more detailed evolution of the FT-IR spectra upon heating is illustrated in Figure 4.
The carbon deposition can be correlated with the drastic impedance drop to almost metallic
conductivity in the EIS measurement at ~1040 K due to the presence of a conducting distorted
graphitic carbon layer\(^9\), which is not detached upon re-cooling the sample. This course of
reaction is also reflected in the corresponding FT-IR measurements. Especially above 1073 K
the growth of the carbon layer is visible by a drastic transmittance decrease. At 1123 K a
remaining relative transmittance of ~20% and almost no transmittance is left at 1143 K (also
apparent in Figure 4). Also upon cooling, the course of the impedance measurements is
exactly followed by the corresponding FT-IR spectra, which in accordance with the
impedance do not show substantial changes, especially no spectral features of methane.
Figure 3

Electrochemical impedance spectroscopy measurement on Y$_2$O$_3$ in dry CH$_4$ (flow ~0.7 ml s$^{-1}$) at linear heating and cooling rates of 10 K min$^{-1}$ up to 1173 K and back to 470 K (large panel). For these measurements an excitation signal of 20 mV and a frequency of 1 Hz were used. Reprinted with permission in part from Chem. Mater. 26 (2014) 1690. Copyright 2014 American Chemical Society. The correlating FT-IR spectra were also performed at a flow rate of 0.7 ml s$^{-1}$ up to 1143 K and back to 470 K at linear heating and cooling rates of 10 K min$^{-1}$.
The summarized progressive change in the methane fingerprints on Y$_2$O$_3$ upon heating the sample to very high temperatures is shown in Figure 4. It basically comprises all the important features also visible in the EIS signal.

![Figure 4](image)

**Figure 4**
Overview of FT-IR spectra on Y$_2$O$_3$ collected in flowing CH$_4$ (flow $\sim$ 0.7 ml s$^{-1}$) at linear heating rates of 10 K min$^{-1}$ up to 1143 K.

For the volumetric adsorption studies (Figure 5) Y$_2$O$_3$ was treated in 90 mbar CH$_4$ and the mass spectrometer signals of CH$_4$, H$_2$, CO$_2$ and CO were measured$^9$. Similar to the EIS experiment the carbon deposition starts at 1070 K, indicated by a strong decrease of the CH$_4$ mass spectrometer signal. In contrast to the experiments with flowing methane, the FT-IR spectra are conventionally shown in absorbance as there is no pronounced decrease of the transmittance. This is due to the fact that 90 mbar CH$_4$ are not enough to form a continuous conducting carbon layer. However, the mass spectrometer signals show the formation of CO and CO$_2$ above 600 K (see enlarged inset). FT-IR spectroscopic measurements should in principle allow not only the detection of CO and CO$_2$, but also those of possible reaction intermediates. It has been shown in a previous publication, that part of the methane is...
decomposed into carbon, which subsequently forms CO/CO$_2$. Part of the methane is also directly converted to carbon oxides. FT-IR spectroscopic measurements should in principle help to discriminate these two features (Figure 6). We emphasize also at this stage that for this direct correlation absolutely dry conditions are a pre-requisite, as the carbon layer is very sensitive to moisture, which would lead to partial detachment. Both Figure 5 and Figure 6 show the versatility of the setup to ensure this ultra-purity under static conditions. CO$_2$, CO, CH$_4$ and the OH region were marked in Figure 6. The right side panel of Figure 6 convincingly shows that the gas-phase CO$_2$/CO features appear in the FT-IR spectra at more or less the same temperature as in the volumetric adsorption experiment. Due to the significant weaker infrared absorption of CO compared to CO$_2$, the CO signal is much weaker and finally becomes only significantly visible at higher gas phase concentrations.
Volumetric adsorption measurement of 90 mbar CH$_4$ on Y$_2$O$_3$ up to 1273 K with a linear heating rate of 10 K min$^{-1}$. The mass spectrometer signals of CH$_4$, H$_2$, CO$_2$ and CO are shown. Reprinted with permission in part from Chem. Mater. 26 (2014) 1690. Copyright 2014 American Chemical Society. The correlating FT-IR spectra were also performed in a static CH$_4$ atmosphere of 90 mbar up to 1143 K at a linear heating rate of 10 K min$^{-1}$.

Figure 6
Summarized FT-IR spectra of Y$_2$O$_3$ in static 90 mbar CH$_4$ at a linear heating rate of 10 K min$^{-1}$ up to 1143 K.

IV. Summary
The discussed examples clearly demonstrate that the parameter-range of the operando FT-IR setup could be drastically enhanced by the use of the newly constructed high-temperature, ambient pressure quartz reactor cell approach combined with a highly pure gas supply. This setup provides both the possibility to perform highly specific infrared experiments in transmission mode and offers at the same time the great advantage to directly follow and hence to correlate experiments performed by other in-situ/operando methods such as electrochemical impedance spectroscopy, volumetric adsorption or even catalytic investigations. None of these methods provides spectroscopic information, hence the
necessity to use a FT-IR reaction cell compatible to these experimental conditions, which are easy to obtain for these methods, but very demanding for spectroscopic measurements. FT-IR and Raman spectroscopy are the only comparably easy and accessible tools for these purposes. However, severe restrictions apply to the latter method, as in-situ or even operando measurements are very demanding due to the detection of the scattered light. Especially the huge temperature range and the opportunity to deliberately control the moisture and hydroxylation degree facilitate a wide range of applications in the field of gas-solid systems, such as catalytic studies. Furthermore, the quartz reactor and sample holder ensure that in the heated region no side reactions caused by additional metal or ceramic components can occur and all physico-chemical changes can be reliably referred to the sample. As has been shown, this is of crucial importance for e.g. oxide systems, whose surface chemistry and especially hydroxylation degree have a huge impact on the nature of adsorbates and reactivity, even more at high temperatures. We note that studies of that kind require a sophisticated setup to achieve ultra-dry/pure conditions.

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Supporting Information

Figure S1

In-situ collected FT-IR spectra following static adsorption of CO$_2$ on pure Y$_2$O$_3$ at room temperature and pressures from 8x10$^{-6}$ mbar up to 10 mbar taken with the previous setup used in ref. 8.
References

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36. Supplementary Material Figure S1, panels A and B