

Operando-DRIFTS Investigations for Identifying the Active Phase
of RuO₂ and IrO₂ in the CO and CH₄ Oxidation Reaction

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“Now, as to myself, I have so described these matters as I have found them and read them; but if anyone is inclined to another opinion about them, let him enjoy his sentiments without any blame from me”
Flavius Josephus

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Kurzzusammenfassung

Katalytische Prozesse werden in der Industrie von der Synthese bis zur Abgasbehandlung weitläufig eingesetzt. Daher hat die Entwicklung neuer Katalysatoren einen tiefgreifenden Einfluss auf diese Prozesse und bietet das Potenzial, Produktivität und Effizienz zu steigern. Die in dieser Arbeit untersuchten Katalysatoren sind RuO_2 und IrO_2 . Frühere Studien haben gezeigt, dass sie trotz ihrer ähnlichen Kristallstruktur und Nähe im Periodensystem unterschiedliche Aktivitäten in den Oxidationsreaktionen von CO und CH_4 zeigen. Der Vergleich der Unterschiede und Gemeinsamkeiten erlaubt Rückschlüsse auf die katalytische Funktionsweise beider Materialien. Da insbesondere reduzierbare Oxide unter Reaktionsbedingungen anfällig für Veränderungen sind, ist es notwendig die Analyse unter operando-Bedingungen durchzuführen. Zu diesem Zweck wurde ein operando-DRIFTS-Reaktor konstruiert, der es ermöglicht, den Umsatz in Verbindung mit IR-Spektren zu messen. Um Informationen über den Zustand des Katalysators zu erhalten, wurde CO als Sondenmolekül verwendet. Ru und Ir in ihrer oxidischen, metallischen und teilweise reduzierten Form mit TiO_2 als Träger wurden diversen Reaktionsbedingungen ausgesetzt. Durch diesen Ansatz konnten charakteristische Absorptionsbanden identifiziert werden, die anzeigen in welchem Oxidationszustand der Katalysator vorliegt. Durch die Korrelation der Umsatzkurven mit den CO-Banden konnten Schlüsse auf die aktivste Phase sowie die Reaktionsmechanismen gezogen werden. Bei der CO-Oxidation zeigen sowohl RuO_2 als auch IrO_2 die höchste Aktivität für die jeweils teilweise reduzierten Proben. Für RuO_2 ist bekannt, dass die Oberfläche unter Reaktionsbedingungen Phasenseparation in oxidierte und reduzierte Bereiche durchläuft. Die Positionen der CO-Banden konnten diesen Phasen zugeordnet werden, wobei CO im Grenzbereich zwischen den Phasen die höchste Aktivität zeigt. Es konnte ebenfalls gezeigt werden, dass die Oberfläche von RuO_2 auch unter oxidierenden Reaktionsbedingungen Reduktion erfährt. Da dies für IrO_2 nicht beobachtet wurde und die teilweise reduzierten Katalysatoren aktiver sind, könnte dies die überlegene Aktivität von RuO_2 bei der CO-Oxidationsreaktion erklären. Für IrO_2 wurde festgestellt, dass teilweise reduziertes IrO_2 erheblich aktiver in der CH_4 -Oxidation ist, als oxidiertes IrO_2 . Allerdings verarmt die Oberfläche unter reduzierenden Bedingungen an Sauerstoff, was die Aktivität bei hohen Temperaturen beeinträchtigt. Daher ist teilweise reduziertes IrO_2 unter oxidierenden Bedingungen am aktivsten. Darüber hinaus konnte gezeigt werden, dass die Methanoxidation auf teilweise reduziertem IrO_2 über ein formaldehydartiges (H_2CO) Zwischenprodukt verläuft, im Gegensatz zum formiatartigen (HCO_2) Zwischenprodukt, welches in der früheren Literatur für vollständig oxidiertes IrO_2 gefunden wurde.

Abstract

Catalytic processes are widely used in industry from synthesis to waste treatment. Hence, the development of new catalysts has profound impact on these processes bearing the potential to increase productivity and efficiency. The catalysts studied in this work are RuO₂ and IrO₂. Those two were chosen as previous studies have shown that, despite their similar crystal structure and proximity on the periodic table, they exhibit somewhat different activity in the oxidation reactions of CO and CH₄. A comparison of similarities and differences allows to draw conclusions about the workings of both materials. As catalysts, especially those consisting of reducible oxides, are prone to change under reaction conditions, it is necessary to perform the catalytic studies under operando conditions. For this purpose, an operando DRIFTS reactor was constructed that allows the conversion to be measured in conjunction with IR spectra revealing the surface species present on the catalyst. In order to gather information about the state of the catalyst CO was utilized as a probe molecule. To establish the complex relations of band position and shape to surface state of the catalyst, Ru and Ir were prepared in their fully oxidic and metallic form as well as a partially reduced oxide using TiO₂ as a support. By using this approach, in conjunction with ex situ XPS, band patterns could be established that were used to distinguish the oxidation state of the catalyst. Correlating the conversion curves to the CO bands observed, the most active phase as well as reaction mechanisms could be deduced. In case of CO oxidation both RuO₂ and IrO₂ revealed an improved activity for the partially reduced samples with respect to their fully oxidized counterparts. For RuO₂ the surface is known to undergo phase separation into oxidized and reduced areas and CO band positions could be assigned to these phases with CO in the boundary region between these phases showing the highest activity. It could also be shown that the surface of RuO₂ undergoes some reduction even under oxidizing reaction conditions. As this is not observed for IrO₂ and the partially reduced catalysts were more active, this may explain the superior activity of RuO₂ in the CO oxidation reaction. For IrO₂ it was also found that it is significantly more active towards CH₄ oxidation in its partially reduced than its fully oxidized form. However, under reducing conditions the surface was depleted of oxygen, thus hampering the activity at high temperatures. Hence, IrO₂ was most active in its partially reduced form under oxidizing conditions. Here the partially reduced IrO₂ will slowly oxidize, subsequently losing its activity advantage. Furthermore, it could be shown that the methane oxidation on partially reduced IrO₂ proceeds through a formate-like (H_yCO) intermediate, as opposed to the formate-like (H_yCO₂) intermediate found for fully oxidized IrO₂ in previous studies.

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List of Abbreviations

AFM	Atomic Force Microscopy
CER	Chlorine Evolution Reaction
DRIFTS	Diffuse Reflectance Infrared Fourier Transform Spectroscopy
IR	Infrared
Ir _{cus}	Coordinatively unsaturated Ir in IrO ₂
RG	Reactive Gas
RoVi	Rotational Vibrational
MFC	Mass Flow Controller
MS	Mass Spectrometry
OER	Oxygen Evolution Reaction
O _{br}	Oxygen in bridge position
O _{ot}	Oxygen in on-top position
Ox-	Fully oxidized sample
Red-	Partially reduced sample
Ru _{cus}	Coordinatively unsaturated Ru in RuO ₂
XPS	X-Ray Photoemission Spectroscopy
XRD	X-Ray Diffraction

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1 Introduction

1.1 Motivation and Outline

Catalysis plays a pivotal role in the industrial sector, enabling efficient and sustainable processes. While it is challenging to provide an exact number of processes in the chemical industry that employ catalysis due to the wide range of applications, it is safe to say that catalysis is extensively used across various sectors.¹ Therefore, the development and optimization of catalysts is a major research topic influencing many aspects of how and what chemicals are produced. The choice of catalyst can determine how much energy is needed, what selectivity is achieved and how stable a given process is. Catalyst research can be done, generally speaking, either by screening or rational design. Screening in this context means to test a wide variety of catalytic systems until one with improved performance is found, while the rational design approach tries to predict the best catalyst a priori based on a mechanistic understanding of the system. In order to gain such mechanistic understanding, it is necessary to elucidate what surface sites, reactants and intermediates are involved in the reaction. However, many catalysts dynamically change under reaction conditions, forming active sites that are no longer present after the reaction has been concluded. This dynamic behavior is especially prevalent with reducible oxides of precious metals, which are used in many catalytic processes.²⁻⁹ Therefore, ex situ or even in situ analysis is often insufficient to gain insights into the mode of operation of a catalyst. This necessitates the employment of analytics while the catalyst is under reaction conditions, so-called operando analysis. Methods typically employed for operando analysis are X-ray diffractometry (XRD), X-ray photoelectron spectrometry (XPS), atomic force microscopy (AFM), Infrared (IR) spectrometry and Raman spectrometry.¹⁰⁻¹²

In heterogeneous catalysis the reaction generally takes place on the surface of a solid catalyst, while the reactants are in the gaseous or liquid phase. The mechanism is, therefore, governed by the state of the catalyst surface and the adsorbates present on it. As such, it is necessary to utilize methods that are surface-sensitive and provide information about both of these aspects. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) first and foremost probes the adsorbate species. This allows for identification of reaction intermediates present on the surface during the reaction. Furthermore, molecular vibrations of some adsorbed molecules are dependent on the site they are adsorbed onto. Utilizing this dependency, it is possible to deduce the state of the catalyst by analyzing the band position

and shape of certain adsorbates. The molecule mostly used for this purpose is CO, as its vibrational frequency is strongly dependent on the electron density at the adsorption site.^{13–15} For these reasons the present thesis employs operando DRIFTS coupled with on-line mass spectrometry (MS) to gain insights about the catalytic reactions described in **Section 1.2**. Here DRIFTS provides information about the state of the catalyst and surface species, while MS provides conversion data. By correlating these two datasets it is possible to elucidate the most active phase of the catalysts as well as reaction mechanisms.

1.2 Investigated Catalytic Reactions

The reactions studied in the present thesis are the CO oxidation on RuO₂ and IrO₂ as well as methane oxidation on IrO₂. CO oxidation was studied because it is a supposedly simple reaction that has been widely investigated for a multitude of catalysts. Despite its apparent simplicity, CO oxidation provides a plethora of fundamental insights into catalytic processes and serves as an ideal model reaction for studying heterogeneous catalysis. One of the primary reasons for using CO oxidation as a benchmark reaction is its well-studied kinetics and reaction mechanisms.^{2,3,16–20} At the same time the reaction mechanism may depend on factors such as oxidation state of the catalyst, surface coverage, presence of other adsorbates and temperature. This in turn allows researchers to elucidate the behavior of a catalyst in various states and under differing reaction conditions. These behaviors may then be extrapolated to other more complex and industrially relevant reactions.

For RuO₂ these processes include oxygen evolution reaction (OER) in electrochemical water splitting^{21,22}, electrochemical chlorine evolution reaction (CER)²³ or the catalytic HCl oxidation (Deacon process)^{24–26}. The investigation of the CO oxidation reaction on RuO₂ has led to three main interpretations of what constituted the most active phase: (1) metallic Ru with CO and O reacting as chemisorbed species without oxidizing the metal^{17,27–29}, (2) oxidized RuO₂ with CO binding to coordinatively unsaturated Ru sites (Ru_{cus}) and reacting with adjacent bridging O^{30–34} and (3) a sub-stoichiometric RuO_x or mixture of phases. The main mechanistic arguments in this discussion revolve around the Sabatier principle. In this context metallic Ru is argued to be inactive due to oxygen binding too strongly at low O coverages and CO binding too weakly at high O coverages.^{3,35–37} RuO₂ on the other hand is argued to undergo CO poisoning due to its high CO adsorption energy, with a reaction order of -1 being predicted.³ This prediction has not turned out to be accurate, as a reaction order of +1 was demonstrated for CO and O for the CO oxidation over RuO₂(110).³⁸ Lastly, the

coexistence of multiple phases needs to be considered. Increased activity of Ru catalysts for the CO oxidation reaction was linked to the presence of ultra-thin RuO₂ or sub-stoichiometric RuO_x layers over Ru metal.^{35,38–41} Blume *et al.*⁴² demonstrated by XPS microscopy that oxidized and reduced areas coexist on Ru(0001) under CO oxidation reaction conditions and linked this coexistence to increased activity. A more in-depth discussion of previous studies on the active phase of RuO₂ can be found in **Publication I**.

Although the CO oxidation on IrO₂ has been significantly less well studied than for RuO₂, its study may also allow insights into the functioning of this material. As both materials crystallize in the rutile structure and are close on the periodic table some parallels in their behavior are to be expected. IrO₂ as well RuO₂ revealed high activity in the CER⁴³ and OER^{44,45} reactions. Previous studies found, however, that the two materials exhibit significantly different activities in the CO and CH₄ oxidation reaction. RuO₂ was found to be more active in the CO oxidation reaction, while IrO₂ exhibited superior activity in the CH₄ oxidation reaction. Therefore, studying both materials and comparing similarities and differences may provide insights into their respective behavior.

Thus, the behavior of IrO₂ in the CO oxidation may shed light on its characteristics, which help explore its mechanisms in more industrially relevant reactions like the combustion of alkanes. IrO₂ has proven to be a good catalyst for the combustion of methane^{46,47} and propane⁴⁸. These alkanes are themselves greenhouse gases more potent than CO₂. They are released into the environment, besides natural sources, by natural gas engine exhaust and gas heaters. Methane in particular has proven to be very difficult to catalytically oxidize.^{49,50} The development of efficient catalysts for the exhaust treatment may, therefore, significantly reduce the environmental impact of the combustion of these gases. Another reason why the catalytic oxidation of methane is of interest, is its conversion into value-added chemicals by partial oxidation.^{51,52} In order to allow for a rational design of a catalyst that does not fully oxidize methane to CO₂, it is necessary to gain mechanistic insight.

1.3 Experimental Approach

1.3.1 Operando DRIFTS in Heterogeneous Catalysis

Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) measures the infrared radiation diffusely reflected off the surface of a solid powder sample, rather than directly transmitted through it, as is common with traditional infrared techniques. Due to this aspect of DRIFTS, it is highly sensitive to adsorbates present on the surface of the investigated material. The technique also requires only little sample preparation. As long as the sample is sufficiently reflective no further treatment such as pressing of pellets is required. In the context of heterogeneous catalysis these properties of the technique facilitate its application in an operando setting. The use of the untreated powder sample in DRIFTS allows reactants to flow through the catalyst layer in the same manner as they would in a plug flow reactor. Since the reactions in heterogeneous catalysis take place on the surface of the material, the surface sensitivity of DRIFTS is advantageous for detecting surface adsorbates relevant to the investigated reaction. Therefore, operando DRIFTS can be a powerful technique to elucidate various aspects of a heterogeneously catalyzed reaction, such as identifying adsorbates and their respective reactivity, differentiating between reaction intermediates and spectator species, catalyst oxidation state and reaction mechanisms. Means of detecting the oxidation state of the catalyst are established in this thesis by systematically exposing the metallic, oxidized or partially reduced catalyst to CO. This was done in conjunction with ex situ XPS to establish the oxidation state of the catalyst. The position and shape of the CO adsorption bands measured by DRIFTS could then be correlated to the oxidation state as measured by XPS. This in turn allows for the identification of the catalyst oxidation state under operando conditions by DRIFTS, for which the oxidation state cannot be verified by XPS.

In DRIFTS research, CO is widely used as a probe molecule to provide information about various aspects of the catalyst such as alloy composition⁵³, particle size⁵⁴, coverage³⁴ and oxidation state^{55–57}. The significance of CO as a probe molecule largely stems from its unique properties, specifically, its capacity to bind with various transition metals and its characteristic vibrational modes. A key aspect of its utility as a probe molecule lies in its ability to interact with a catalyst's surface, with the π -backbonding mechanism playing a crucial role. The interaction of CO with a transition metal catalyst involves the overlap of the filled d-orbitals of the metal with the π^* antibonding orbital of CO. This back-donation process leads to the strengthening of the metal-CO bond, concomitant with the weakening of

the C-O bond. The weakening of the C-O bond directly influences the vibrational behavior of the CO molecule, particularly in terms of the C-O stretching mode. As the strength of the C-O bond decreases due to π -backbonding, the vibrational frequency of the C-O stretching mode decreases, leading to a red shift in the IR absorption spectrum. This shift in the absorption frequency is directly indicative of the strength of the metal-CO bond, which in turn provides a measure of the catalyst's surface state. For example, if a catalyst is more oxidized there will be less electrons available for the π -backbonding. This in turn will lead to the C-O bond remaining stronger and, therefore, the corresponding C-O-stretching vibration will occur at a higher wavenumber. In the same way degree of surface coverage and co-adsorption of other species will influence the band positions as they change the local electron density. While the sensitivity of band positions of the adsorbed CO molecule can be a great asset, the multitude of possible influences can also render interpretation difficult.

1.3.2 Pitfalls of DRIFTS

Despite its many advantages DRIFTS experiments also bear a multitude of pitfalls stemming from various aspects of the technique. starting from reactor design over sample preparation to data treatment. Firstly, the windows used in DRIFTS reactors are not resistant to high temperatures. In order to keep the windows cool, commercial DRIFTS reactors contain gaps between the heated sample and the reactor walls, thus introducing large gas volumes into the reactor. Reactors containing large gas volumes allow for back-mixing of the reactant gases. If this occurs the reactor will no longer behave like a plug flow reactor and the measured conversion data will be distorted. This issue can be alleviated by using high flow rates.⁵⁷ However, high flow rates can disturb the catalyst layer creating bypasses. This is more of an issue in DRIFTS reactors as in other types of reactors, as the top of the catalyst bed has to be exposed to allow for IR radiation to interact with the sample. Therefore, no supporting material like glass wool can be put on top of the sample and the catalyst bed is less constrained.

Another issue is that of accurately measuring the sample temperature. Most commercial DRIFTS cells use a thermocouple embedded in the sample holder to record the catalyst temperature. Li *et al.*⁵⁸ demonstrated that this leads to inaccurate temperature measurements, as these cells exhibit large temperature gradients throughout the catalyst layer. For the Harrick® cell it was found that the temperature of the surface of the catalyst was 100 °C

below the value measured by the thermocouple, when the temperature was set at 460 °C. These gradients are, however, more manageable at temperatures below 300 °C.^{57,59,60} The use of gases with high thermal conductivity like H₂ and He exacerbate the problem, since the top of the catalyst layer gets cooled more efficiently by the incoming gas. The spectra recorded in DRIFTS represent the upper layer of the catalyst bed in accordance with the path length of the IR radiation in the sample. In order to obtain temperature data, that correspond better to the DRIFT spectra, a pyrometer can be used instead of a thermocouple. This has the advantage that both the pyrometer as well as the DRIFTS collect their data using IR radiation from the top of the sample. Therefore, both temperature data and IR spectra stem from the same probed volume.

In terms of sample preparation there are also multiple things to consider. If the investigated sample is highly absorbing in the investigated spectral range, an insufficient amount of the incident IR radiation is being reflected to facilitate analysis. To mitigate this problem, it is common to mix the sample with a reflective matrix akin to the dilution of a sample in a solvent or KBr in transmission IR spectroscopy.⁶¹ Alkali halides, commonly used as matrix for solid samples in transmission IR spectroscopy, are known to affect the reactivity of heterogeneous catalysts.⁶² For this reason, non-absorbing but inert materials like MgO, Al₂O₃, SiC and SiO₂ are commonly used in operando DRIFTS. It is important to choose a suitable matrix material as some may change under reaction conditions due to changes in temperature, oxidation or hydration state.⁶³ SiC for example readily forms oxides on the surface and may not be suitable for reactions investigated under oxidizing conditions.⁵⁷ Silica materials exhibit backbone vibration overtones in the commonly investigated wavenumber region of 1800-2000 cm⁻¹, which are sensitive to temperature and hydration state changes and may distort the baseline.⁶³ On the other hand, these absorption bands can also be used to normalize the optical path length for quantification purposes.

Data treatment is essential for receiving reliable information from DRIFTS. As for other types of IR spectroscopy, it is necessary to record a background spectrum to distinguish the absorption bands of the apparatus and matrix from those of the surface species and catalyst. It is possible to simply use the pure matrix material at room temperature as a blank. However, this may cause some issues as the matrix material may change its reflective and absorption behavior depending on the temperature. If the background spectrum is then used for correction of the catalyst's spectra under reaction conditions, the resulting corrected spectrum will be skewed or show adsorption bands stemming from the support. This issue

can be mitigated by using the investigated mixture of catalyst material and matrix itself and record background spectra for all investigated temperatures under inert conditions. In doing so, the sample should be pretreated by heating to ensure no surface species are present before background spectra are recorded. Subsequently, background spectra at the investigated temperatures are recorded under inert atmosphere. It is still possible that the background is unstable during the reaction as the catalyst material adapts to these conditions. This may be caused by the material being oxidized or reduced, resulting in a change of its reflective properties. If catalyst loadings are small, background distortions and intensity changes are generally manageable. Still, comparisons of band intensities between different catalyst states are not straightforward as the optical path length changes with varying reflectivity. In some cases, this issue can be mitigated by employing a background vibration band to normalize intensities.

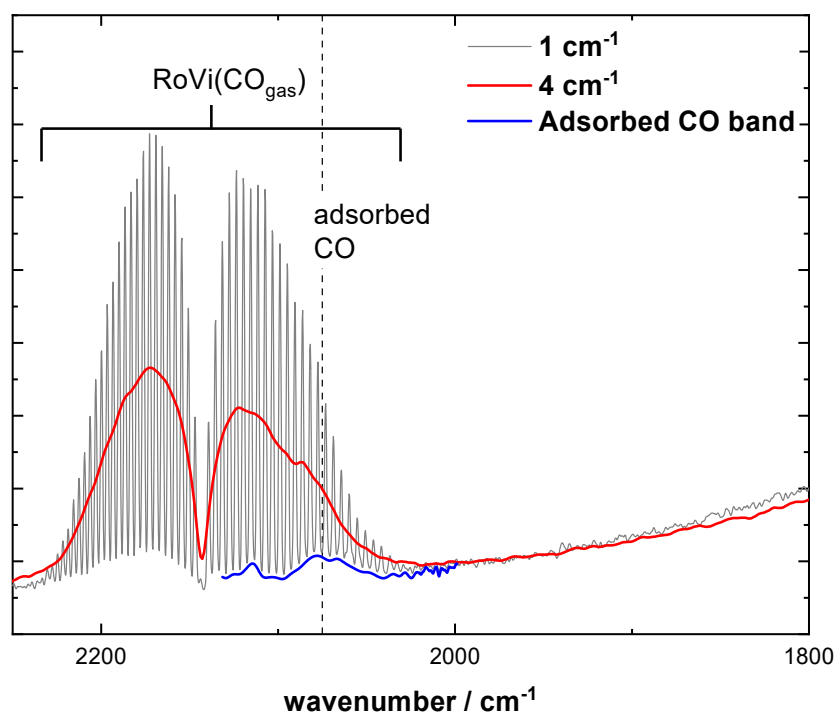


Figure 1: DRIFT spectra of CO adsorbed on a catalyst surface recorded with high (1cm⁻¹; grey) and low (4 cm⁻¹; red) resolution. In the low-resolution spectrum, the band of adsorbed CO cannot be clearly distinguished. In the high-resolution spectrum, the minima of the RoVi spectrum of gaseous CO allow for identification of the band of adsorbed CO (blue).

Oftentimes the absorption bands of adsorbed species appear in the same wavenumber region as their counterparts in the gas phase. This overlap becomes an issue if the species in

question is a reactant and is present in high concentrations in the gas above the catalyst. Under these conditions weak absorption bands are hard to make out and may be missed. One solution to this would be the subtraction of the gas phase signal from the spectrum. However, the gas phase spectra vary with temperature due to the differing occupancy of rotational and vibrational states as well as differing concentrations due to conversion. With temperatures and concentrations of reactants along the optical path through gas volume and catalyst layer being non uniform, predicting the shape and intensity of the signal is no longer feasible. An alternative to this is to record the spectra under reaction conditions with a high resolution. In theory the absorption between rotational lines should be zero. Therefore, the absorption at these minima corresponds to the spectrum without the gas phase species. If the spectrum in question is recorded with a sufficiently high resolution one is able to recognize weak absorption bands this way. A comparison of high- and low-resolution spectra, containing a weak band of adsorbed CO as well as CO in the gas phase, is shown in **Figure 1**.

1.4 Reactor design

For the DRIFTS measurements a reactor setup was designed and build. The reactor is capable of precise temperature control as well as quick gas exchange. The cell was designed to allow for pressures of up to 20 bars in order to study reactions under industrially relevant conditions.

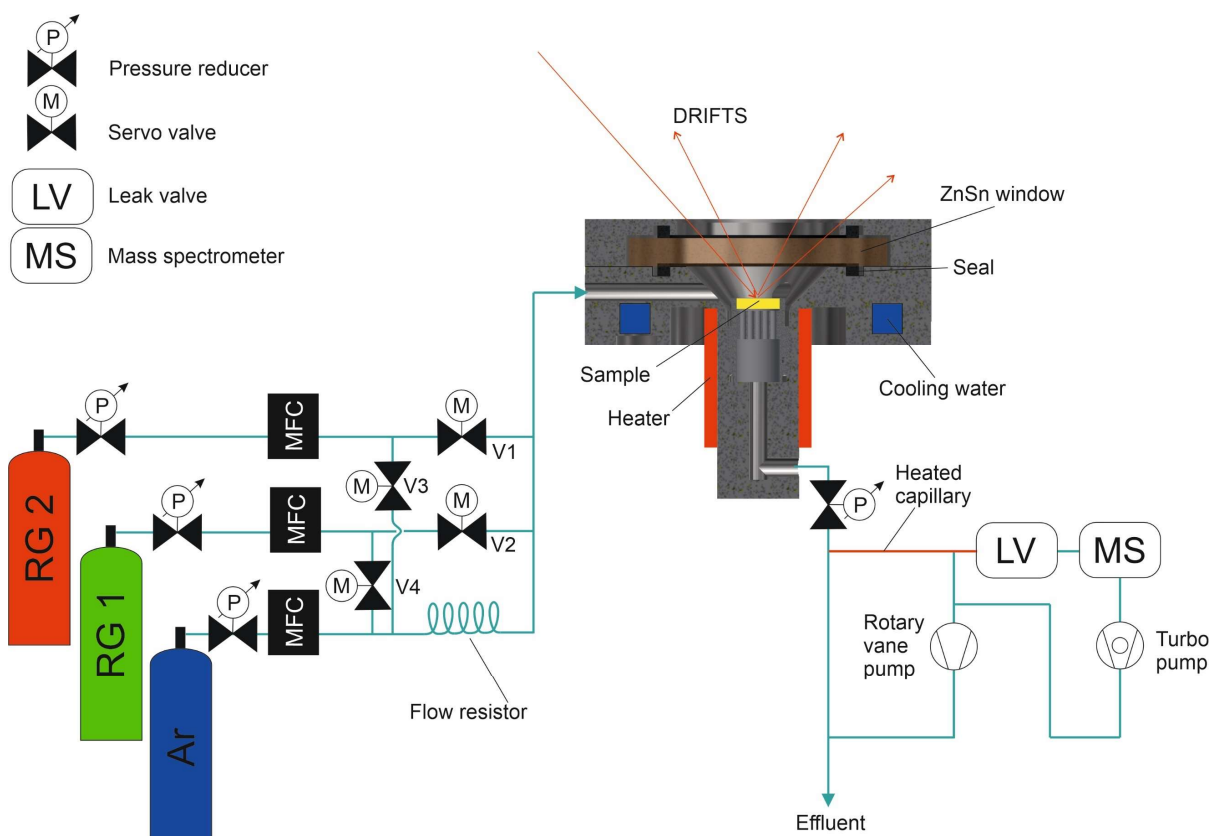


Figure 2: Scheme of the reactor setup with gas supply and analytics. The green lines represent steel tubes. The red arrows show the IR light striking the sample. Reactive gases are denoted as RG 1 and RG 2. The outer dimensions of the reactor cell are 55 mm in diameter and height. The catalyst bed (yellow) is 7 mm in diameter and 3 mm high.

The apparatus, shown in **Figure 2**, can be divided into the following 4 segments:

1.4.1 Gas supply

The gas supply consists of gas bottles with pressure reducers, which feed mass flow controllers (MFCs). All tubing consists of stainless steel with an inner diameter of 1 mm to

reduce dead volume and facilitate a quick gas exchange. The carrier gas (argon) is connected upstream, as it has the highest flow rate. The carrier gas will pass by the T-junctions where the other reactive gases are connected, ensuring quick mixing and transport of the gases with lower flowrates.

If a reactive gas was in use and is shut off, it would take up to a few hours for the residual gas to diffuse out of the tubing that connects the outlet of the MFC to the carrier gas line. For this reason, it is necessary to flush the connecting line with argon after the gas is no longer needed. To allow the flushing procedure, a flow resistor, consisting of 8 m coiled 1 mm inner diameter tubing, is introduced behind the carrier gas MFC. Between the MFC and the flow resistor a tube is attached, connecting to the line between the respective reactive gas MFC and carrier gas line downstream. Electronically controlled valves are located after the connection point of this tube on the carrier gas line (**Figure 2**; denoted as V1/V2) as well as on the tube itself (**Figure 2**; denoted as V3/V4). The valves are servo actuated as opposed to solenoids, as the latter would introduce pressure spikes during activation that disturb the catalyst bed. As long as a reactive gas is in use the respective valve V1/V2 is open, while the corresponding V3/V4 is closed. When the gas is to be shut off, V3/V4 is opened and the flow of the reactive gas is stopped by the MFC. Due to the flow resistor the main part of the carrier gas is redirected through the reactive gas lines, flushing out any remaining reactive gas. After 15 seconds both V1/V2 and V3/V4 are closed, completing the gas shut off procedure.

If CO is used as reactive gas additional treatment is needed. Under high pressures CO forms tetracarbonylnickel $\text{Ni}(\text{CO})_4$ with the Ni from the steel gas bottle. This carbonyl has a significant vapor pressure at room temperature and is carried with the CO gas into the reactor. If it then encounters temperatures above ca. 160 °C it decomposes and deposits nickel. As nickel itself is a highly active catalyst in many reactions this has to be prevented. Therefore, a so-called copper trap is used. It consists of 20 m copper tubing with an inner diameter of 3 mm, heated to 230 °C, through which the CO flows before entering the MFC. This ensures any $\text{Ni}(\text{CO})_4$ is decomposed before entering the reactor.

1.4.2 Reaction cell

The reaction cell is composed of the main body, sample cup, ZnSe-window, and clamping ring for the window. All metal parts were made from 1.4742 steel, which is a nickel-free high-temperature steel. Ni-free steel is used to ensure that the reactor is not itself an active catalyst.

One design aspect of the reactor is its small internal volume in order to facilitate a quick gas exchange. This is important as a large dead volume may cause conversion data to be distorted.⁵⁷ The largest volume of the reactor is located above the catalyst. To ensure an even gas flow there are three gas inlets positioned 120° from one another. After the gas enters it flows through the sample and sample holder followed by a 3 mm bore. The bore was chosen relatively large to allow for easier cleaning of the reactor body.

Due to the compact build the heated parts of the cell are close to the ZnSe-window. In order to make sure the window is not damaged by excessive heat a cooling channel is situated in the upper part of the main body. A significant part of the heating power is absorbed by the cooling water, making a heater capable of up to 300 W necessary. An early version of the reactor used a mineral-isolated heating wire (*ThermoExpert*) glued to the shaft of the main body with high-temperature steel glue (*Durabond 954, Polytec PT*). This setup allowed for sample temperatures up to 400 °C. However, proved to be unreliable as the glue cracked and the heating wire melted after some time. The final iteration used a nozzle heater band (*Ihne&Tesch*). This version was more reliable but could only reach sample temperatures of 340 °C. The outside of the heater was isolated using stone wool held in place by a steel clamp. The temperature was controlled with a PID controller (*2416, Eurotherm*).

The sample holder (**Figure 3**) is designed in a way that good contact with the heated stem is ensured while contact with the cooled parts of the body are minimized. In order to achieve this the upper third of the holder was turned down to a smaller diameter. This makes sure that the lower part with the thread has good connection with the heated walls, while the upper part does not contact the cooled parts of the main body wall.

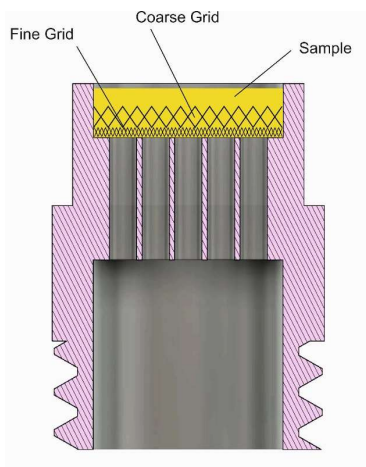


Figure 3: Cross-sectional view of the sample holder with grids. The fine grid stops the sample from falling through. The sample is pressed lightly into the coarse grid placed on top of the fine grid. This stabilizes the sample laterally against the formation of gas bypasses.

The sample is placed in the top of the sample holder, where a 2 mm deep cup was milled out. To ensure an even gas flow throughout the catalyst layer the bottom of the sample cup is perforated with 1 mm holes. On top of these a fine steel grid (500 mesh) is placed to keep the catalyst powder from falling into the reactor. To be able to measure DRIFTS, no material can be placed on top of the catalyst layer to fixate it, as it is common with plug flow reactors. For this reason, it is possible for the gas flowing through the sample to disturb the catalyst layer, creating bypasses. In order to mitigate this another coarse grid (50 mesh) is placed on top of the fine grid. The catalyst powder is then placed loosely on top and lightly compressed with a plunger of 0.1 mm depth. This procedure results in a catalyst layer stable enough to withstand the gas flow while still not hindering it. The typical amount of catalyst used in this work is 30 mg. The sample holder is then screwed into the main body as shown in **Figure 2**. The gas flows from the top to the bottom of the sample holder, to best utilize the stabilizing effect of the grids.

1.4.3 Optics

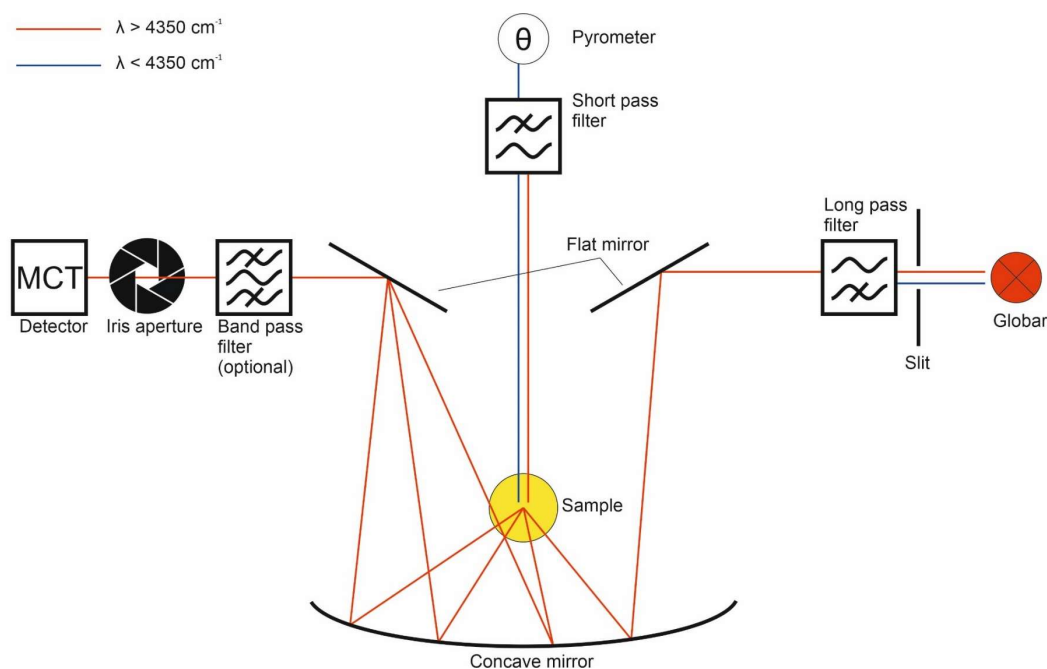


Figure 4: Scheme of the beam path of the DRIFTS-apparatus. General parts of the spectrometer are not shown for clarity reasons. Radiation with a wavelength of less than $2.3\ \mu\text{m}$ are shown in blue with those above $2.3\ \mu\text{m}$ shown in red.

The optics of the DRIFTS apparatus comprise a “Vertex 70V” spectrometer from *Bruker* and a “DiffIR” module from *Pike*. A scheme of the optical path is shown in **Figure 4**. The “DiffIR” module is placed in the sample compartment of the spectrometer and flushed with nitrogen to ensure a background spectrum clear of water or CO_2 from the air. The interferometer compartment of the spectrometer is evacuated for the same reason. The light, created by a globar, is directed onto the sample through a series of mirrors. Here the light is diffracted from the powder sample, at which point absorption from the surface molecules under investigation occurs. The diffracted light is then refocused by a concave mirror placed above the sample. The refocused light is then directed by another set of mirrors to a Mercury-Cadmium-Telluride (MCT) detector. To ensure that the detector is not oversaturated an iris aperture is placed in front of it, limiting the light reaching the detector. Likewise a band pass filter can be placed in front of the detector, to only allow wavelengths in the investigated region to pass.

The temperature of the sample is measured by a pyrometer. This pyrometer is sensitive to wavelengths around $2.3\ \mu\text{m}$. However, light in this wavelength region is not only produced by the heated sample but also by the globar. To make sure the pyrometer only measures light

produced by the heated sample a long and a short pass filter is used. The long pass filter is placed directly behind the globar filtering all wavelength below 2.3 μm . The long pass filter is placed in front of the pyrometer filtering all wavelength above 2.3 μm . This way only light created by the heated sample with a wavelength below 2.3 μm reaches the pyrometer, enabling temperature measurements.

1.4.4 Gas Analytics

The gas analytics setup is shown in the right side of **Figure 2**. In order to analyze the effluent gas a heated capillary is attached to the tube exiting the reactor. The other side of the capillary is attached to a T-connector that is held under vacuum by a rotary vane pump. This will draw about 10 sccm of the effluent gas through the capillary ensuring continuous and quick exchange of the gas in the T-connector. On the other side of the T-connector a leak valve is placed, that lets a small amount of gas pass into the main vacuum chamber housing of the mass spectrometer (*Pfeiffer* QMG 220).

2 Results and Discussion

2.1 Preparation and Analysis of Oxide and Metal Samples as References for the Assignment of Band Positions

In order to gain a deeper understanding of the active phase of IrO₂ and RuO₂, firstly the CO oxidation reaction was investigated as a benchmark reaction. The main challenge in case of both materials was to assign the observed absorption bands to the various catalyst states and adsorption sites thereon. For this reason, samples containing the respective pure metal and pure oxide were prepared. As the pure catalyst materials do not exhibit sufficient reflectivity on their own, it is necessary to use a reflective matrix for DRIFTS measurements. Therefore, oxide RuO₂ and IrO₂ samples were prepared as supported particles on TiO₂ via the Pechini method. The details of the synthesis are described in **Publication II**. The same preparation was previously used by Khalid *et al.*⁴⁶ thus allowing for comparison with previous datasets. A simple physical mixture would also provide a matrix for DRIFTS measurements and would reduce any potential influences of the supporting material. However, when physically mixing two powders, agglomerates remain within the mixture. These agglomerates negatively impact reflectivity as they trap light entering them. Harsh mixing procedures like ball milling may alleviate this issue but bear the possibility of changing the sample via mechanochemistry. The loading of the oxides was chosen to be 2 mol%, so samples would retain sufficient reflectivity, while still containing enough active material for investigation. After the Pechini preparation the samples are shown by XPS to be purely oxidic (cf. **Figure 5A-B**). These samples are referred to as ox-RuO₂@TiO₂ and ox-IrO₂@TiO₂, respectively. For best comparability of the oxide and metal samples the latter should be derived by complete reduction from the former. However, even when the supported oxide samples were exposed to strongly reducing conditions (4% H₂ in Ar) at up to 600 °C for 24 h, XP spectra still show oxide signals and thus no pure metal could be obtained. In order to allow for the investigation of pure metal samples it was necessary to employ commercially available metal Ir⁰ (*abcr*) and Ru⁰ (*chempur*) powders physically mixed with TiO₂. These samples are referred to as Ir⁰+TiO₂ and Ru⁰+TiO₂ respectively. Here a loading of 33 w% was necessary to obtain sufficient signal strength. After reductive pretreatment to remove surface oxides that may have formed by contact with air, the samples are shown to be purely metallic by XPS (cf. **Figure 5C-D**).

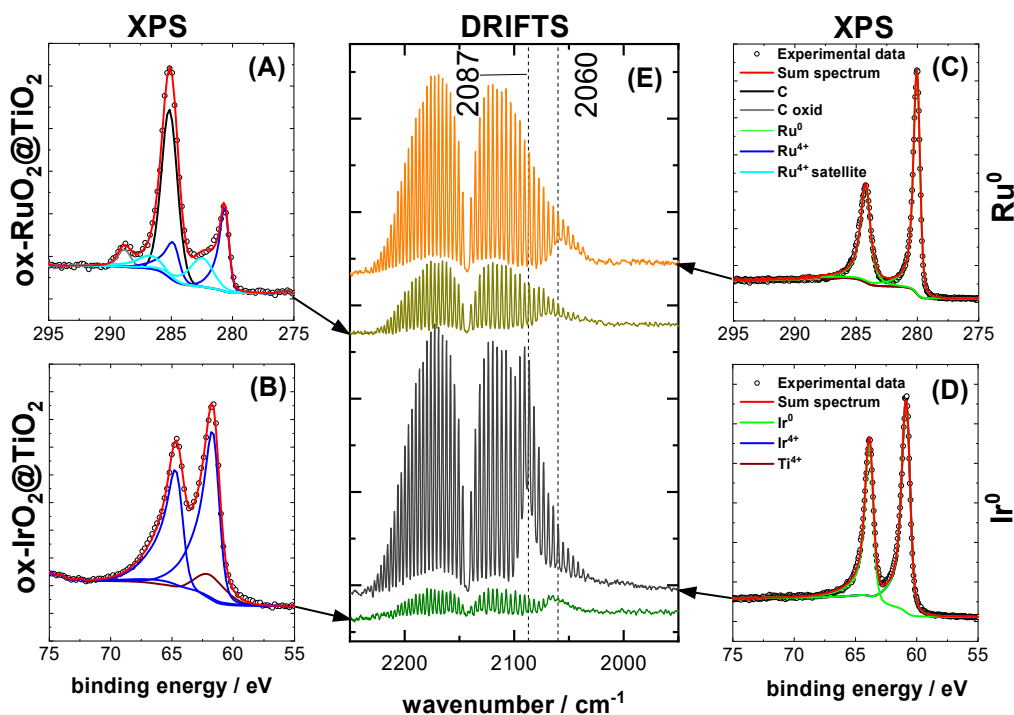


Figure 5: XP spectra in the Ru 3d and Ir 4f region, respectively, of (A) metallic Ru⁰, (B) fully oxidized ox-RuO₂@TiO₂, (C) metallic Ir⁰ and (D) fully oxidized ox-IrO₂@TiO₂ as well as (E) the corresponding DRIFTS spectra of CO adsorbed on these samples. The legends shown in the right XP spectra are valid for both Ru and Ir XP spectra, respectively. The XP spectra of metallic samples were recorded without the TiO₂ support to obtain sufficient signal strength.

The purely metallic and purely oxidic samples were then exposed to a CO-containing gas feed in the DRIFTS reactor. For all cases only a single symmetric absorption band is observed (cf. **Figure 5E**). For Ru⁰ and RuO₂ this band is positioned at ca. 2060 cm⁻¹, while for Ir⁰ and IrO₂ the band is positioned in the range of 2060 to 2087 cm⁻¹. The presence of only one band is rather surprising, as particles exhibit different surface facets providing different absorption sites. This observation points toward dipole-dipole coupling occurring between the vibrational mode of all sites. This behavior has previously been reported for RuO₂(110).³⁰ It was, therefore, concluded that discrimination of purely metallic and purely oxidic surfaces on band position alone is not possible for these materials. When exposed to reaction conditions, however, both IrO₂- and RuO₂-based samples exhibit more complex DRIFT spectra, that allow deeper insights into the functioning of both catalysts.

2.2 CO Oxidation on RuO₂

RuO₂@TiO₂ demonstrates a more complex DRIFTS band pattern upon partial reduction, as opposed to the single symmetric band observed for the ox-RuO₂@TiO₂ and Ru⁰+TiO₂ samples. When RuO₂@TiO₂ and Ru⁰+TiO₂ were heated in a reducing atmosphere (1% O₂/ 4% CO/95% Ar) to 300 °C they as well were partially reduced and oxidized, respectively, according to XPS. The partially reduced samples are called red-RuO₂@TiO₂. Partial reduction of the ruthenium-based catalysts results in a shoulder appearing on the 2060 cm⁻¹ band stretching to lower wavenumbers, as well as a high-wavenumber signal at 2135 cm⁻¹ in DRIFTS (cf. **Figure 6** blue spectrum). The low-wavenumber shoulder consists of multiple bands that are made out to behave independently. Those bands appear at ca. 1985-2030 cm⁻¹, 2040 cm⁻¹ and 2075 cm⁻¹. In order to investigate the relation between the CO surface species and activity, conversion curves for oxidized and reduced RuO₂@TiO₂ samples were recorded under reducing and oxidizing CO oxidation reaction conditions. For both conditions the red-RuO₂@TiO₂ shows higher conversion throughout the investigated temperature range up to 260 °C. The conversion curves exhibit various features that can be correlated with changes in DRIFT spectra. For RuO₂@TiO₂ under oxidizing conditions the singular band at 2075 cm⁻¹ remains largely unchanged till it is no longer observable above 140 °C due to CO reacting off the surface too quickly. A representative spectrum is shown in grey in **Figure 6**. In the corresponding conversion plot a plateau, in which the conversion only marginally increased, is observed between 140 and 180 °C. No conclusion regarding the nature of the plateau could be drawn at this point, due to CO not being observable in DRIFTS under oxidizing conditions at high temperatures. However, when ox-RuO₂@TiO₂ is cooled down again, while still maintaining the oxidizing feed composition, the low-wavenumber signals denoting partial reduction appear below 140 °C (cf. **Figure 6**; red spectrum). Furthermore, under reducing conditions ox-RuO₂@TiO₂ shows a similar conversion plateau. Contrary to under oxidizing conditions, under reducing conditions the surface CO remains observable throughout the entire temperature region. Here it can clearly be seen that the end of the plateau is correlated with the appearance of the low-wavenumber signals at around 200 °C, with the 2040 cm⁻¹ band being the most dominant. Based on these spectra it seems RuO₂@TiO₂ was reduced, which in turn is correlated with an increase in conversion. This reduction occurred even when an oxidizing feed was applied. This behavior may explain why RuO₂ is more active in the CO oxidation reaction than IrO₂ under oxidizing conditions.⁶⁴

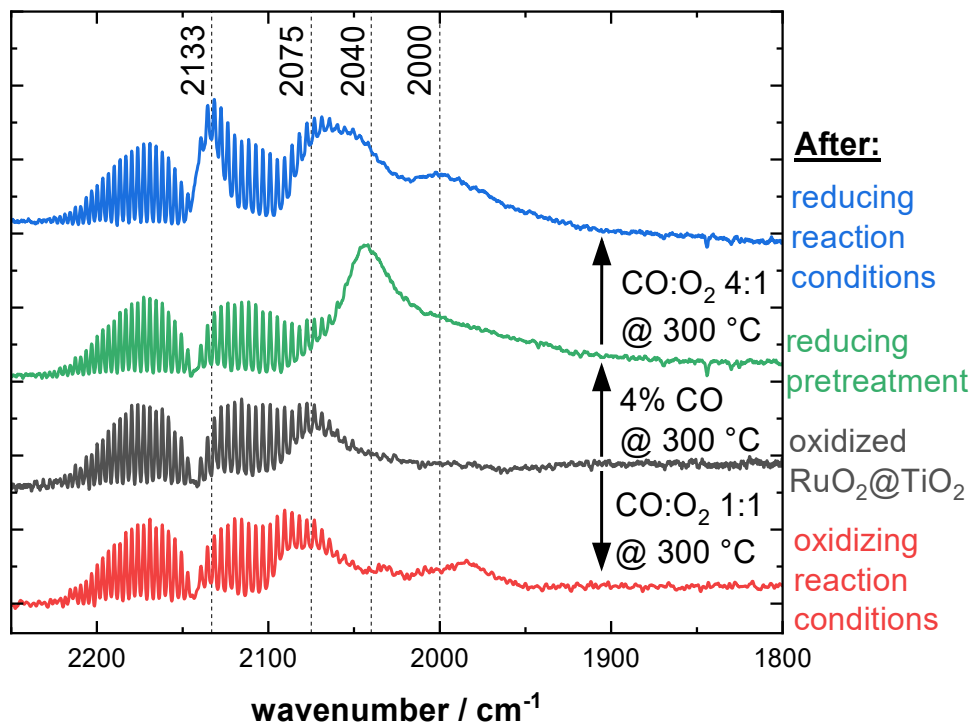


Figure 6: DRIFT spectra of $\text{RuO}_2@\text{TiO}_2$ in its fully oxidized state (grey) exhibiting one symmetric band, after reducing pretreatment (green) showing additional low-wavenumber bands with the 2040 cm^{-1} band being most dominant, after reducing reaction conditions (blue) exhibiting the same signals as after reducing pretreatment but with the 2075 cm^{-1} and 2133 cm^{-1} being more dominant and after oxidizing reaction conditions (red) showing a similar band pattern to that after reducing reaction conditions but with the 2075 cm^{-1} signal being more dominant.

On red- $\text{RuO}_2@\text{TiO}_2$, directly after the reducing pretreatment, the 2040 cm^{-1} band is the most dominant at first, with shoulders reaching down to higher and lower wavenumbers corresponding to the 2075 and $1985\text{--}2035\text{ cm}^{-1}$ bands (cf. **Figure 6**; green spectrum). Under oxidizing conditions, the 2040 cm^{-1} band remains stable up to $60\text{ }^\circ\text{C}$, at which point it starts to diminish, while the 2075 cm^{-1} band becomes more dominant. This change correlates with the conversion starting to increase. At $100\text{ }^\circ\text{C}$ the conversion curve exhibits a sharp increase at which point the 2040 cm^{-1} band disappears almost completely. With subsequent temperature increase the low wavenumber bands keep decreasing in intensity, denoting a

progressing oxidation of the catalyst, till above 200 °C only the 2075 cm⁻¹ band remains. The 2040 cm⁻¹ band disappearing first is interpreted as this species being the most reactive. This interpretation is further corroborated by the increase in activity at 200 °C for ox-RuO₂@TiO₂ under reducing conditions coinciding with the appearance of the dominant 2040 cm⁻¹ signal.

Regardless of its initial state, RuO₂@TiO₂ will adapt to the reaction conditions, which is further illustrated by ox-RuO₂@TiO₂ and red-RuO₂@TiO₂ being exposed to oxidizing and reducing reaction conditions for a second reaction cycle. Here, DRIFT spectra as well as conversion curves converge for reducing and oxidizing conditions, respectively. After the second cycle under reducing conditions, the DRIFT spectra exhibit bands at 2135 cm⁻¹ and 2075 cm⁻¹ with a low-wavenumber shoulder incorporating the 2040 and 2000 cm⁻¹ bands. The conversion curves of the second cycle only exhibit a small residue of the plateau and match closely with the first reaction cycle of the red-RuO₂@TiO₂ under reducing conditions. After the second cycle under oxidizing conditions, in DRIFTS the 2075 cm⁻¹ band is dominant with some low-wavenumber shoulder being observable. The conversion curves still exhibit the plateau in the 140 -200 °C region, however, the overall conversion is shifted up rather significantly compared to the first cycle of ox-RuO₂@TiO₂ under oxidizing conditions. Again, this suggests that the catalyst has undergone reduction, while being exposed to oxidizing conditions.

The surface of RuO₂ is known to segregate into oxygen-rich and oxygen-depleted phases.^{30,42,65} The observed bands in DRIFTS can be correlated to the different surface phases by considering their behavior in conjunction with these previous studies on the RuO₂ surface chemistry. The band in the region of 1985-2030 cm⁻¹ changes its shape and position in accordance with the state of the catalyst. When the catalyst is reduced it exhibits a broad asymmetric shape, reaching down to low wavenumbers. This points towards CO being adsorbed on an inhomogeneous surface providing a range of adsorption sites, resulting in a range of wavenumbers. As RuO₂ gets more oxidized the band becomes more symmetric, while shifting to higher wavenumbers. The latter is expected, when more oxygen is introduced into the vicinity of CO. These bands becoming more symmetric is in line with the partially reduced surface, initially providing a range of adsorption sites, but becoming more homogeneous with increasing degree of oxidation. The 2075 cm⁻¹ band may be ascribed to CO on oxide RuO₂ or metal Ru. Considering the reaction conditions under which this band is observed here, it most likely corresponds to oxidized RuO₂ surfaces in this case. The 2135 cm⁻¹ band has previously been identified as a Ru-carbonyl species Ru^{x+}(CO)_y on

reduced RuO₂(110) by Gao *et al.*³. Here, it was suggested that the interaction between the Ru metal and RuO₂ could significantly influence CO oxidation on RuO₂. The increased activity on a partially reduced RuO₂ surface might indicate a bifunctional behavior akin to what has been observed for PdO. Weaver *et al.*⁴ suggested that, on a partially reduced PdO, CO oxidation is optimally facilitated on the metal Pd surface, which receives oxygen from the adjacent PdO. This bifunctional behavior of the partially reduced RuO₂ aligns with the discussion points of too strong or weak adsorption of CO and O on Ru and RuO₂, respectively (cf. **Section 1.2**). Such boundary areas between oxidized and reduced surface phases might present adsorption sites with intermediate adsorption energies, which, based on the Sabatier principle, would be beneficial for CO oxidation. The CO species related to the 2040 cm⁻¹ band is shown to be especially active. A finding that suggests this band corresponds to CO adsorbed in the boundary region between oxygen-rich and -depleted surface phases. In summary the observed DRIFTS bands were assigned as follows:

- I. 1985–2030 cm⁻¹: CO on partially reduced RuO₂ with shape and position changing according to the surface composition
- II. 2040 cm⁻¹: CO located possibly in the boundary region between surface phases with the highest activity.
- III. 2075 cm⁻¹: CO on oxide RuO₂.
- IV. 2135 cm⁻¹: carbonyl Ru^{x+}(CO)_y, which can form on highly under-coordinated Ru^{x+} sites. Reduced RuO₂ has been demonstrated to roughen^{66,67}, which would provide such under-coordinated Ru^{x+} at the edges and corners³.

2.3 CO Oxidation on IrO₂

Similar to RuO₂@TiO₂, for IrO₂@TiO₂ a drastic change of the CO adsorption band in DRIFTS is observed, as reducing reaction conditions are applied. After both the IrO₂@TiO₂ and Ir⁰+TiO₂ samples were heated in a reducing atmosphere (1% O₂/4% CO/95% Ar) to 300 °C a broad shoulder stretching from the original band position of 2085 cm⁻¹ down to 1800 cm⁻¹ is observed for both samples. XPS reveals that after this treatment both samples are in a state of partial reduction or oxidation respectively. This leads to the conclusion that a partially reduced IrO₂ surface can be identified in DRIFTS by this broad shoulder of the CO adsorption band. This information can then be used to monitor the oxidation state of the catalyst in relation to its activity under reaction conditions. In doing so, the IrO₂@TiO₂ was

pretreated under oxidizing or reducing conditions by exposing it to 4% CO or 4% O₂, respectively, at 300 °C. Partially reduced samples are referred to as red-IrO₂@TiO₂ and oxidized samples as ox-IrO₂@TiO₂. The pretreated samples were then heated to 300 °C under reducing (1% O₂/4% CO/95% Ar) and oxidizing (2% O₂/2% CO/96% Ar) CO oxidation reaction conditions. Distinct correlations can be derived between the conversion and the oxidation state of the catalyst as monitored by MS and DRIFTS.

Regardless of the reaction conditions being oxidizing or reducing, red-IrO₂@TiO₂ exhibits higher activity. This can be seen by the reaction onset temperature being about 50 °C earlier for red-IrO₂@TiO₂. After the reaction onset, red-IrO₂@TiO₂ retains a higher conversion for the entire temperature range and reaches full conversion 60 °C and 40 °C earlier than ox-IrO₂@TiO₂ under oxidizing and reducing conditions, respectively. Correlations between the activity of the sample and the appearance or disappearance of the broad shoulder in DRIFTS, indicating the partial reduction of IrO₂@TiO₂, could be seen at various points. For ox-IrO₂@TiO₂ under reducing conditions, the activity increases steeply at 180 °C, concomitantly with the appearance of the broad shoulder in DRIFTS (cf. **Figure 7**). Correspondingly, for red-IrO₂@TiO₂ a similar increase in activity is observed at 140 °C with the broad shoulder disappearing, while leaving the 2077 cm⁻¹ oxide signal behind. The latter observation may suggest, that the catalyst got oxidized at this point accompanied by an increase in activity, thus contradicting the previous interpretation. However, when the catalyst is cooled down again from 160 °C under the same reaction conditions the shoulder band reemerges. Therefore, the disappearance of the shoulder band at higher temperatures points towards the corresponding CO species being more active than those represented by the 2077 cm⁻¹ band. This leads to the more active species reacting off and not being observable in DRIFTS, while the less reactive CO species adsorbed on the more oxidized parts of the catalyst can still be observed. The spectra for ox-IrO₂@TiO₂ under oxidizing conditions and red-IrO₂@TiO₂ under reducing conditions remained largely unchanged, indicating that the catalyst is stable under these conditions.

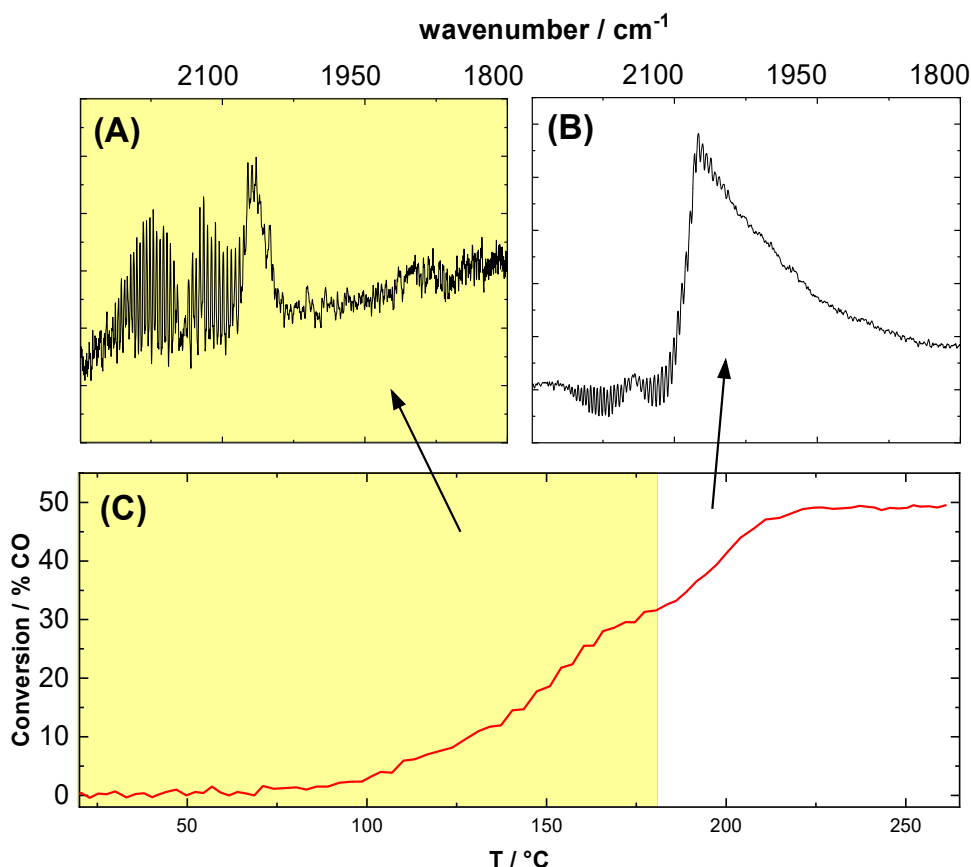


Figure 7: DRIFT spectra of ox-IrO₂@TiO₂ under reducing reaction conditions (A) before reduction occurred showing one symmetric signal and (B) after reduction occurred showing a broad shoulder band, as well as (C) the corresponding conversion curve. The conversion curve exhibits a slowdown in conversion increase around 160 °C. After this point reduction is accompanied by an uptick in conversion.

Overall, these results demonstrate that IrO₂ adapts dynamically to the reaction conditions, with the partially reduced red-IrO₂@TiO₂ exhibiting superior activity for the CO oxidation reaction. Considering that RuO₂ and IrO₂ both occur in the rutile structure, and given the proximity of Ru and Ir on the periodic table, it is suggested that a similar mechanism for heterogeneous CO oxidation catalysis as observed on RuO₂ might be applicable to IrO₂. On RuO₂ CO oxidation proceeds as follows^{30,31}: (1) CO adsorbing on the catalyst surface; (2) CO combining with O from the oxide lattice to produce CO₂; (3) CO₂ desorbing; and (4) the resulting O vacancy in the oxide lattice being refilled with O₂ from the gas phase. Considering IrO₂, its increased activity when being reduced could then be attributed to a couple of factors. First, the lattice oxygen in partially reduced IrO₂ is potentially easier to extract, due to its lower binding energies. Additionally, the presence of a defect-rich lattice might result in

oxygen being more mobile, allowing active sites to be resupplied with oxygen more rapidly. This perspective aligns with recent findings by Martin *et al.*⁷, which highlighted the role of subsurface oxygen replacing surface oxygen in methane oxidation on IrO₂.

2.4 CH₄ Oxidation on IrO₂

The insights gained from the CO DRIFTS experiments on IrO₂ were subsequently applied to the CH₄ oxidation reaction. The focus of this study was to elucidate the influence of the catalyst's oxidation state on its activity. The as-prepared IrO₂@TiO₂ samples were pretreated at 300 °C under 4% O₂ or 4% CH₄ to obtain fully oxidized (ox-IrO₂@TiO₂) or partially reduced (red-IrO₂@TiO₂) samples, respectively. These samples were then heated under 4% CH₄ as well as reducing (1% CH₄ / 1% O₂ / 98% Ar) or oxidizing (1% CH₄ / 4% O₂ / 95% Ar) reaction conditions, while recording conversion data and DRIFT spectra.

The conversion curves of ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ reveal that under both reducing and oxidizing conditions the red-IrO₂@TiO₂ exhibits significantly higher conversion than ox-IrO₂@TiO₂. Furthermore, if the catalyst is exposed to multiple reaction cycles the conversion curve will adapt to the reaction conditions: during the second cycle ox-IrO₂@TiO₂ under reducing conditions will show a conversion curve previously observed for red-IrO₂@TiO₂ and vice versa, while ox-IrO₂@TiO₂ under oxidizing conditions and red-IrO₂@TiO₂ under reducing conditions will remain stable. However, for the partially reduced catalyst under reducing conditions the conversion will be significantly hampered at temperatures above 240 °C. This results in the conversion of both red-IrO₂@TiO₂ and ox-IrO₂@TiO₂ being equal to 37% at 330 °C under reducing and oxidizing conditions, respectively. On the other hand, when red-IrO₂@TiO₂ is exposed to oxidizing reaction conditions no hampering of conversion occurs and a conversion of 57% at 330 °C is achieved. (cf. **Figure 8A**). This points towards red-IrO₂@TiO₂ being depleted of surface oxygen under reducing conditions, thus not being able to facilitate high conversions. While the oxidizing feed will supply sufficient oxygen to maintain high conversion, it will also oxidize the catalyst deactivating it in the process. The hampering of activity under reducing conditions can be further understood considering the findings of Martin *et al.*⁷ and Kim *et al.*⁶⁸. They reported that oxygen adsorbed on top (O_{ot}) of coordinatively unsaturated Ir (Ir_{cus}) is especially reactive. At the same time the conversion of O_{ot} to oxygen in bridge positions (O_{br}) is facile.⁶⁹

Consequently, on an oxygen-depleted surface any O_{ot} would quickly transform into less active O_{br} resulting in a decreased activity.

The higher activity of red- $IrO_2@TiO_2$ can be understood when considering C-H bond cleavage on transition metal oxides being dependent on the cooperative interaction of coordinatively unsaturated metal ions and adjacent oxygen.^{70–76} Partially reduced IrO_2 provides a large number of cus-sites due to surface oxygen being abstracted, while still providing a sufficient amount of surface oxygen sites to take up the abstracted hydrogen.

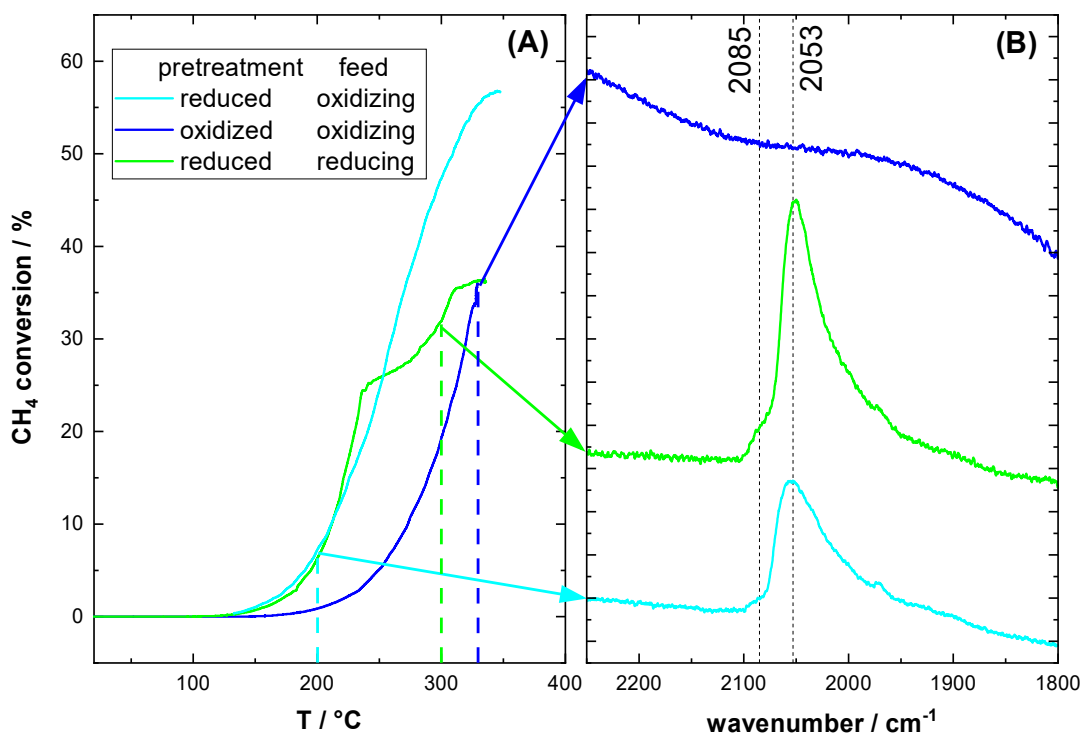


Figure 8: (A) conversion curves of ox- $IrO_2@TiO_2$ under reducing and oxidizing conditions as well as red- $IrO_2@TiO_2$ under oxidizing conditions. (B) corresponding DRIFT spectra showing the CO adsorption region. The colored arrows and dashed lines denote at what point the spectra were taken. For the reduced samples this corresponds to the first appearance of a CO band. For the oxidized sample under oxidizing conditions no CO band was observed.

Insights into the reaction mechanism of CH₄ oxidation on red- $IrO_2@TiO_2$ and ox- $IrO_2@TiO_2$ can be deduced from the DRIFT spectra. When the $IrO_2@TiO_2$ samples are exposed to oxidizing or reducing reaction conditions no surface species are observed in the CO band region below 200 °C in DRIFTS. Surface CO signals are, however, present in DRIFTS at higher temperatures for all samples and conditions except for ox- $IrO_2@TiO_2$

under oxidizing conditions. Representative spectra are shown in **Figure 8B**. When a CO signal is present the band always exhibits a broad shoulder reaching down to lower wavenumbers, indicating that IrO₂ is in a state of partial reduction, according to the results discussed in **Section 2.3**. When CO is observed under reaction conditions the 2085 cm⁻¹ band, here likely indicating oxidized surfaces of IrO₂, is only a small shoulder signal with the main band being positioned at lower wavenumbers. Together with the finding that CO is only present on the surface when DRIFTS indicates a reduced surface, this points towards CO generation being restricted to partially reduced surfaces. The CO observed on oxidized IrO₂ surfaces likely originates from CO desorbing from reduced and readsorbing onto oxidized surfaces.

Methane oxidation over heterogeneous catalysts may proceed through multiple pathways that can be characterized by the sequence of hydrogen abstraction and oxygen addition. In the first mechanism, only one oxygen is added before all hydrogen is abstracted and a formaldehyde-like intermediate (H_yCO) and subsequently CO is formed. In the second mechanism a second oxygen is added before the abstraction of the last hydrogen, generating a formate-like intermediate (H_yCO₂). In the latter case no CO can be formed. For CO to be observable it has to be created at a rate comparable to its conversion to CO₂. As IrO₂ is also an efficient catalyst for the oxidation of CO⁶⁴ the rate of CO production has to be high. Consequently, since CO is observable the formaldehyde pathway is dominant on partially reduced IrO₂. Previous studies by Martin *et al.*⁷⁷, performed on single-crystalline IrO₂(110), found that the reaction proceeds preferentially through the formate (H_yCO₂) intermediate. This is not in conflict with the data presented here, as the IrO₂(110) was shown not to be reduced. Furthermore, Martin *et al.*⁷⁷ observed a steep increase in activity, when the IrO₂(110) was reduced, although no further investigation of the reduced sample was reported. The findings of the present thesis suggest, that the reaction path for the oxidation of methane over IrO₂ is dependent on the oxidation state of the catalyst. On oxidized IrO₂ the formate pathway seems to be dominant, while for partially reduced IrO₂ the formaldehyde pathway is prevalent. Furthermore, the latter reaction pathway seems to facilitate higher activities. This insight may allow for rational design of IrO₂-based catalysts by tuning of their activity and selectivity via altering its oxidation state. This is especially relevant under the aspect of partial oxidation of methane to methanol, which requires formaldehyde as an intermediate.

3 Conclusions and Perspective

This thesis presents studies of the active phases of IrO_2 and RuO_2 in the CO oxidation reaction as a benchmark reaction as well as the active phase of IrO_2 in the CH_4 oxidation reaction. In order to gain these insights an experimental approach comprising operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) coupled with on-line mass spectrometry (MS) was employed. For this purpose, a reactor was built combining these two techniques. The reactor consisted of a gas supply capable of quick gas exchange, a small volume reaction cell allowing optical access to the sample and a quadrupole MS connected to the exit of the reaction cell. DRIFTS was used to identify surface species present on the catalyst materials under reaction conditions. The focus lay on utilizing CO as a probe molecule for identifying the oxidation state of the catalyst under operando conditions. Simultaneously, the conversion was recorded via on-line MS. By correlating the conversion with the state of the catalyst, conclusions could be drawn about the most active phases as well as the reaction mechanisms.

The study of the CO oxidation reaction on RuO_2 supported on TiO_2 ($\text{RuO}_2@\text{TiO}_2$) demonstrates that partially reduced and fully oxidized $\text{RuO}_2@\text{TiO}_2$ can be distinguished by DRIFTS using CO as a probe molecule. Fully oxidized $\text{RuO}_2@\text{TiO}_2$ is characterized by a single symmetric band at ca. 2060 cm^{-1} , while on partially reduced $\text{RuO}_2@\text{TiO}_2$ four band regions are observed. These band regions are assigned to carbonyl $\text{Ru}^{x+}(\text{CO})_y$ (2135 cm^{-1}), CO on oxide RuO_2 (2075 cm^{-1}), CO in a boundary region between surface phases (2040 cm^{-1}) and CO on partially reduced RuO_2 ($2030\text{--}1985\text{ cm}^{-1}$). The conversion data reveals that partially reduced $\text{RuO}_2@\text{TiO}_2$ is more active than its fully oxidized counterpart. The 2040 cm^{-1} CO species is revealed to be especially reactive. This species is likely CO adsorbed in the boundary region between oxidized and partially reduced surface domains, where adsorption energies of CO and O may be favorable according to the Sabatier principle. The catalyst is further shown to dynamically adapt to the reaction conditions independent of its initial state. Especially interesting is the observation of the RuO_2 surface undergoing partial reduction, even when exposed to oxidizing reaction conditions.

In case of the study of the CO oxidation reaction on IrO_2 supported on TiO_2 ($\text{IrO}_2@\text{TiO}_2$), features in DRIFTS were identified that allowed to differentiate between fully oxidized and partially reduced $\text{IrO}_2@\text{TiO}_2$. Here, the fully oxidized $\text{IrO}_2@\text{TiO}_2$ is characterized by a single symmetric band at ca. $2087\text{--}2060\text{ cm}^{-1}$ while partially reduced $\text{IrO}_2@\text{TiO}_2$ is identifiable by a broad shoulder of this band reaching down to 1800 cm^{-1} . The

conversion curves in conjunction with the DRIFT spectra reveal that the partially reduced samples exhibit a significantly higher activity towards the CO oxidation reaction. While the $\text{IrO}_2@\text{TiO}_2$ samples also adapt dynamically to the reaction conditions, no reduction under oxidizing reaction conditions is observed, contrary to $\text{RuO}_2@\text{TiO}_2$. As reduced surfaces are demonstrated to be more active this behavior may explain the superior activity of RuO_2 compared to IrO_2 in the CO oxidation reaction.

The study of the CH_4 oxidation reaction on $\text{IrO}_2@\text{TiO}_2$ utilized the insights derived from the assignment of CO bands in DRIFTS to oxidized or partially reduced $\text{IrO}_2@\text{TiO}_2$. Employing these findings allows for monitoring the oxidation state of the $\text{IrO}_2@\text{TiO}_2$ as long as CO is present on the catalyst surface as an intermediate of the reaction. The conversion curves demonstrate that partially reduced $\text{IrO}_2@\text{TiO}_2$ is more active than its fully oxidized counterpart for the CH_4 oxidation reaction. However, under reducing conditions the conversion is hampered above 240 °C. The highest conversion is reached by partially reduced $\text{IrO}_2@\text{TiO}_2$ under oxidizing conditions. This points towards the samples undergoing oxygen depletion under reducing conditions. Specifically, the more active on-top oxygen (O_{ot}) is likely getting depleted, as the transformation into less active oxygen in bridge positions (O_{br}) is facile on IrO_2 . Further insights on the reaction mechanism are gained from DRIFTS. Whenever CO is observed in DRIFT spectra the band pattern indicates that $\text{IrO}_2@\text{TiO}_2$ is in a partially reduced state. Previous studies, however, demonstrated that CO is not generated on fully oxidized $\text{IrO}_2(110)$ under methane oxidation conditions. In general, the methane oxidation can proceed through two pathways characterized by either a formaldehyde-like (H_yCO) or a formate-like (H_yCO_2) intermediate. The latter would exclude CO as an intermediate. Therefore, the findings of the present study demonstrate the mechanism of CH_4 oxidation on IrO_2 being dependent on the oxidation state of the catalyst. This opens the possibility of tuning the activity and selectivity of IrO_2 -based catalysts by their oxidation state. This tuning may be especially relevant for catalytic processes like the partial oxidation of CH_4 to value-added products like methanol.

4 Publications

4.1 Publication I: Identifying the Active Phase of RuO₂ in the Catalytic CO Oxidation Reaction, Employing Operando CO Infrared Spectroscopy and Online Mass Spectrometry

This study focuses on identifying the most active phase of RuO₂ in the catalytic oxidation of CO. Here, CO serves as a probe molecule for the oxidation state of the catalyst using operando DRIFTS under reaction conditions. As a benchmark metallic Ru⁰ mixed with TiO₂ and fully oxidized RuO₂ supported on TiO₂ were subjected to CO-containing gas feeds. DRIFT spectra recorded under these conditions reveal singular symmetric CO adsorption bands in the region of 2060 cm⁻¹ on both materials. This demonstrates that a clear distinction of purely metallic or oxidic Ru-surfaces is not possible, due likely to dipole-dipole coupling of the adsorbed CO molecules. Partially reducing the RuO₂ or partially oxidizing the Ru⁰ samples results in four band regions emerging in DRIFTS. The RuO₂ surface is known to segregate under CO oxidation conditions into oxidized and partially reduced regions. The band regions are assigned to CO adsorbed on oxidized RuO₂, partially reduced RuO₂, the boundary region between these and carbonyl Ru^{x+}(CO)_y. Partially reduced RuO₂ is shown to be more active than its fully oxidized counterpart with the CO adsorbed in the boundary region being the most active species. Furthermore, it is demonstrated that RuO₂ undergoes partial reduction even when exposed to oxidizing reaction conditions.

H. Over and I devised the experimental schedule. T. Weber and L. Glatthaar performed the XPS measurements. I prepared the samples and performed the DRIFTS experiments. H. Over, and I contributed through scientific discussions of the data. H. Over and I wrote the draft version of the manuscript. All authors revised the manuscript and have given approval to the final version.

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Article

Identifying the Active Phase of RuO₂ in the Catalytic CO Oxidation Reaction, Employing Operando CO Infrared Spectroscopy and Online Mass Spectrometry

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Abstract: Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is combined with online mass spectrometry (MS) to help to resolve a long-standing debate concerning the active phase of RuO₂ supported on rutile TiO₂ (RuO₂@TiO₂) during the CO oxidation reaction. DRIFTS has been demonstrated to serve as a versatile probe molecule to elucidate the active phase of RuO₂@TiO₂ under various reaction conditions. Fully oxidized and fully reduced catalysts serve to provide reference DRIFT spectra, based on which the operando CO spectra acquired during CO oxidation under various reaction conditions are interpreted. Partially reduced RuO₂@TiO₂ was identified as the most active catalyst in the CO oxidation reaction. This is independent of the reaction conditions being reducing or oxidizing and whether the starting catalyst is the fully oxidized RuO₂@TiO₂ or the partially reduced RuO₂@TiO₂.

Keywords: catalytic CO oxidation; ruthenium; RuO₂; catalytically active phase; operando DRIFTS



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1. Introduction

Scientific discussions about the nature of the active phase in a catalytic reaction are not straightforward [1]. This has been encountered particularly often with reducible oxides of precious metals such as Ru [2,3], Pd [4,5], Pt [6], Rh [7], and Ir [8–10], which can readily adapt their oxidation state depending on the specific reaction condition. Therefore, to identify the actual active phase one needs to employ operando spectroscopic or structure-sensitive methods [11–13].

One particular intensively discussed example, and the first catalytic system where this discussion heated up, is the CO oxidation reaction over Ru-based catalysts [14]. Here, two schools are involved: one that prefers metallic ruthenium being the active phase [15] and another that favors oxide being the active phase [16]. We recall that the ruthenium system reveals a surprisingly rich chemistry during CO oxidation, exhibiting phase changes and being subject to poisoning by the formed CO₂ [2] to the point that even oscillations in the CO₂ yield can occur in the CO oxidation reaction performed in a flow cell [17]. At the summit of this discussion, ruthenium dioxide was even considered to be not active at all in oxidation catalysis. Admittedly, the catalytic CO oxidation reaction over Ru-based catalysts does not have application in exhaust after treatment due to the potential formation of toxic and volatile RuO₄ at high temperatures. However, Ru and especially RuO₂ are currently applied in large-scale industrial processes, such as the catalytic HCl oxidation reaction (Deacon process) [18–20] and the electrochemical chlorine evolution reaction (CER) [21], and is considered to be the most efficient oxygen evolution reaction (OER) catalyst for electrochemical water splitting under acidic reaction conditions [22,23]. A general discussion about the catalytically active phase even for a “seemingly less relevant” CO oxidation reaction may therefore have greater impact than hitherto expected, since the

same sites and phases may play a role in these reactions as well. As far as we can judge, the discussion of the active phase of Ru-catalyzed CO oxidation has still not been settled.

In a recent paper by Gustafson et al. [7], the discussion of the active phase in the CO oxidation over Pd and Rh was settled, employing operando high-pressure X-ray photoelectron spectroscopy (XPS). For Rh, the oxygen-covered metallic surface was shown to be more active than the oxide, whereas for Pd, thin oxide films were reported to be at least as active as the metallic surface, but a thicker oxide was less active.

In this contribution, we present and discuss operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments [24,25] in combination with online mass spectrometry for catalytic CO oxidation over ruthenium. Catalytic CO oxidation, a well-documented model reaction [26], is carried out in a flow cell reactor setup under various reaction conditions. DRIFTS has been demonstrated to be a powerful technique to identify reaction intermediates on the catalyst's surface, in particular when CO is involved. More important for our present study is, however, that CO can serve as a versatile probe molecule to study the actual chemical nature of the active phase under reaction conditions [27,28]. This approach is applied to elucidate the active phase of $\text{RuO}_2/\text{TiO}_2$. To do so, first, fully oxidized and fully reduced Ru-based catalysts supported on rutile TiO_2 are prepared. The DRIFT spectra of these are used as reference spectra for the subsequent interpretation of operando CO spectra acquired during CO oxidation under various reaction conditions. It is found that, independent of the reaction conditions, the partially reduced $\text{RuO}_2/\text{TiO}_2$ catalyst constitutes the most active catalyst in the CO oxidation reaction.

2. Experimental Results

2.1. Characterization of Pre-Oxidized and Pre-Reduced $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$ Samples

Figure 1 shows XP spectra of the Ru 3d binding energy region of supported RuO_2 on TiO_2 , referred to as $\text{RuO}_2/\text{TiO}_2$, and the metallic Ru^0 physically mixed with TiO_2 , referred to as $\text{Ru}^0 + \text{TiO}_2$. The fit parameters used were taken from Morgan et al. [29] and are compiled in Table S1. According to the spectra, ruthenium was fully oxidized in the case of $\text{RuO}_2/\text{TiO}_2$. The spectra of the mixture of $\text{Ru}^0 + \text{TiO}_2$ yielded very low signals in XPS. Therefore, pure Ru^0 powder was used to make a meaningful deconvolution possible in the XPS analysis. Here, pure metallic Ru^0 was found. After exposure to reducing CO oxidation conditions (1% O_2 /4% CO/95% Ar), the XP spectra of $\text{Ru}^0 + \text{TiO}_2$ and $\text{RuO}_2/\text{TiO}_2$ in Figure 1 indicate spectral features of both metallic and oxidic Ru. For $\text{Ru}^0 + \text{TiO}_2$, this effect seems to be less pronounced than for $\text{RuO}_2/\text{TiO}_2$. The reason for this is likely the large size of the Ru^0 particles, as only the surface would be oxidized and therefore the bulk metal signal would dominate the XPS signal.

2.2. CO DRIFTS Experiments of Oxidized and Reduced $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$ Samples

Figure 2A shows CO DRIFT spectra of $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$. For this and all following DRIFTS spectra, the y-axis corresponds to absorption in arbitrary units. As evidenced by XPS, these samples consisted of pure oxide and pure metal, respectively. As such, these served as references for assigning spectral DRIFTS features to the CO adsorption on oxide RuO_2 and pure metal Ru^0 , respectively. For both samples, a single symmetric band at around 2060 cm^{-1} was observed. The same spectral feature was observed for $\text{Ru}^0 + \text{TiO}_2$, which had been oxidized in 4% O_2 at $300\text{ }^\circ\text{C}$ (cf. Figure S2). We therefore conclude that a distinction between pure metal and pure oxide cannot be made in DRIFTS experiments based on band position alone.

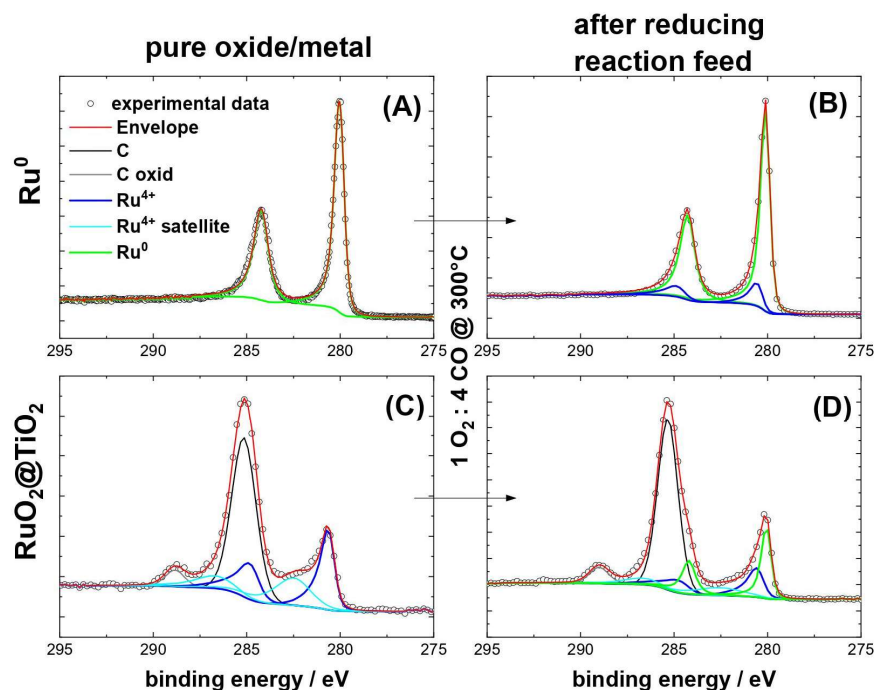


Figure 1. Ru 3d XP spectra of (A) Ru^0 and (C) $\text{RuO}_2@\text{TiO}_2$. The former sample is measured without TiO_2 , as the signal is too weak otherwise. (B,D) show the respective samples after exposure to reducing CO oxidation conditions (1% O_2 /4% CO /95% Ar) at 300 °C. Table S1 provides the fit parameters for deconvolution of the experimental spectra (circles). The fit parameters are taken from Morgan et al. [29].

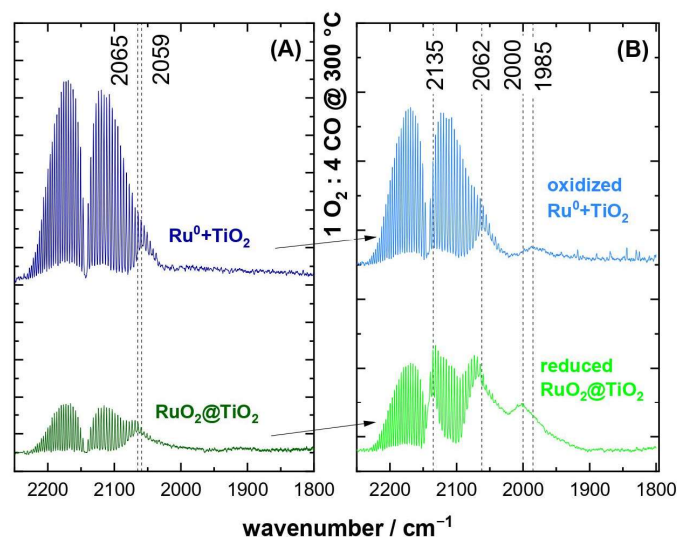


Figure 2. DRIFT spectra of CO adsorption are shown for (A) commercial $\text{Ru}^0 + \text{TiO}_2$ containing only purely metallic Ru and $\text{RuO}_2@\text{TiO}_2$ containing only purely oxidic Ru as prepared by Pechini synthesis on the left. (B) Samples after exposure to reducing CO oxidation conditions (1% O_2 /4% CO /95% Ar) at 300 °C. The spectra are recorded at room temperature.

Under reducing CO oxidation conditions (1% O₂/4% CO/95% Ar) at 300 °C, the as-prepared catalyst changed its composition in that Ru⁰ + TiO₂ partially oxidized, whereas RuO₂@TiO₂ partially reduced. DRIFT spectra of the samples after cooling down under these reaction conditions are summarized in Figure 2B. Here, some differences and similarities of the two samples can be identified. The differences in signal strength were due to differing reflectivity of the samples. For oxidized Ru⁰ + TiO₂ the only difference to the pristine Ru⁰ + TiO₂ was the occurrence of a second absorption band at 1985 cm⁻¹. For RuO₂@TiO₂, the spectra changed more profoundly relative to its pristine sample (Figure 2A). On the one hand, it also exhibited the aforementioned second signal, albeit at a higher wavenumber of 2000 cm⁻¹. In addition, the band at 2065 cm⁻¹ revealed an asymmetric shoulder reaching lower wavenumbers. Experiments on more strongly reduced RuO₂@TiO₂ indicated this shoulder to be a distinct third species at ca. 2040 cm⁻¹ (cf. Figure 3). The importance of this species for the activity of Ru⁰/RuO₂ towards CO oxidation is discussed below. Furthermore, a fourth band at 2135 cm⁻¹ can be observed. Spectra of pure TiO₂ under a CO atmosphere did not indicate any adsorbed CO in DRIFTS (cf. Figure S3). The DRIFT spectra of RuO₂@TiO₂ and Ru⁰ + TiO₂ in Figure 2B under reducing reaction conditions were similar but different from the pristine samples, thus evidencing a partial reduction of RuO₂@TiO₂ and the partial oxidation of Ru⁰ + TiO₂ in Figure 2B.

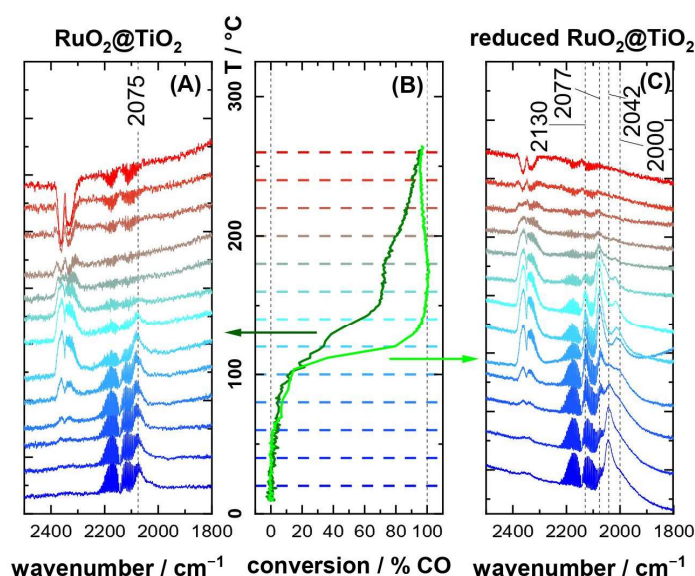


Figure 3. Operando DRIFT spectra of (A) RuO₂@TiO₂ and (C) reduced RuO₂@TiO₂ as well as (B) corresponding CO conversion data under oxidizing (2% O₂/2% CO/96% Ar) reaction feed composition. For the conversion data, the dark green line corresponds to RuO₂@TiO₂ and the light green line to reduced RuO₂@TiO₂. The temperature axis of the conversion plot is marked by dashed lines in the color of the corresponding DRIFT spectra. Spectra are recorded in 20 °C increments. The heating ramp is 1.8 K·min⁻¹.

2.3. CO Oxidation Experiments of RuO₂@TiO₂ Samples

Figure 3 shows DRIFT spectra and the corresponding CO conversion of RuO₂@TiO₂ and reduced RuO₂@TiO₂ (see Experimental Details, Section 4.1) during the CO oxidation reaction under oxidizing conditions (2% O₂/2% CO/96% Ar) in the temperature range of 20 °C to 260 °C.

For RuO₂@TiO₂, presented in Figure 3A, a single band at 2075 cm⁻¹ was observed, in accordance with a fully oxidized RuO₂ surface (cf. Figure 2A). This band remained unchanged in shape and position up to 140 °C, where it started to diminish. Above 160 °C,

no adsorbed CO could be detected in DRIFTS. The conversion increased till it reached a plateau from 150 °C to 180 °C, at which temperature the reaction rate increased again up to 260 °C.

The reduced $\text{RuO}_2/\text{TiO}_2$, which was exposed to 4% CO at 300 °C during the pre-treatment, initially showed, as seen in Figure 3C, a somewhat different peak shape than in Figure 2B. Here the most prominent feature is a band at 2042 cm^{-1} surrounded by shoulders reaching high and low wavenumbers. At 60 °C, the 2042 cm^{-1} signal started to diminish, and at 100 °C it vanished completely. Between 120 °C and 180 °C, the DRIFT spectra looked like those of the reduced $\text{RuO}_2/\text{TiO}_2$ sample (cf. Figure 2B), albeit with a less pronounced low wavenumber shoulder on the 2077 cm^{-1} band. During this transition, it can clearly be seen that the DRIFT bands of adsorbed CO observed between 2100 cm^{-1} and 1980 cm^{-1} consisted of three distinct spectral features at ca. 2075 cm^{-1} , 2000 cm^{-1} , and 2042 cm^{-1} . Although the 2042 cm^{-1} feature vanished first with increasing temperature, the bands at 2075 cm^{-1} and 2000 cm^{-1} seemed to be more stable. It is furthermore important to note that, concomitant with the disappearance of the 2042 cm^{-1} band at 100 °C, the reaction rate increased steeply. Above 100 °C, the conversion observed for reduced $\text{RuO}_2/\text{TiO}_2$ overtook the one for $\text{RuO}_2/\text{TiO}_2$ and remained higher than the one for $\text{RuO}_2/\text{TiO}_2$ over the entire temperature range. At high temperatures, the gas-phase bands of CO and CO_2 seemed to become negative. This is due to IR emission of the heated gas layer above the catalyst.

Figure 4 depicts DRIFT spectra of $\text{RuO}_2/\text{TiO}_2$ during cooling from 260 °C (cf. Figure 3A) to room temperature under an oxidizing (2% O_2 /2% CO/96% Ar) reaction feed. Interestingly, below 160 °C the spectra showed the same low wavenumber bands previously associated with partial reduction of $\text{RuO}_2/\text{TiO}_2$ (cf. Figure 2B), albeit to a lesser degree. This suggests that a partial reduction of the RuO_2 surface is observed, even under an oxidizing reaction feed. Further implications of this finding are discussed in the Section 3.

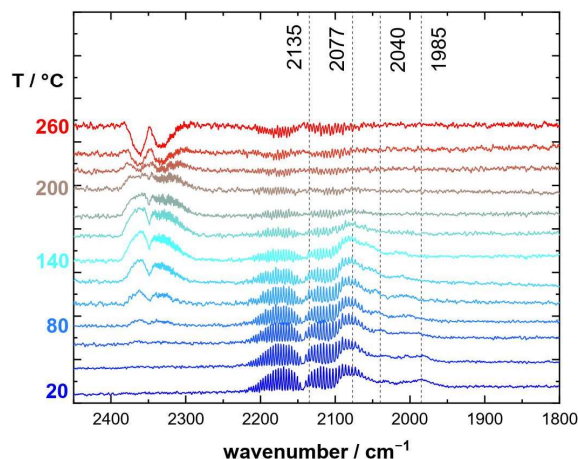


Figure 4. Operando DRIFT spectra of $\text{RuO}_2/\text{TiO}_2$ during cooldown under oxidizing (2% O_2 /2% CO/96% Ar) reaction feed composition. Spectra are recorded in 20 °C increments. The heating ramp is $1.8\text{ K}\cdot\text{min}^{-1}$.

Figure 5 summarizes the operando DRIFTS experiments of $\text{RuO}_2/\text{TiO}_2$ and reduced $\text{RuO}_2/\text{TiO}_2$ during the CO oxidation reaction under reducing conditions (1% O_2 /4% CO/95% Ar) when increasing the reaction temperature from 20 °C to 260 °C together with corresponding CO conversion data. In DRIFTS of $\text{RuO}_2/\text{TiO}_2$ (Figure 5A), there was again only a single band at 2077 cm^{-1} observed at low temperatures. This spectral feature remained unchanged up to 140 °C, when two additional bands appeared at 2025 cm^{-1} and 2134 cm^{-1} . The conversion under reducing reaction conditions (Figure 5B) behaved

like that under oxidizing reaction conditions (Figure 3B), with conversion increasing up to 140 °C, followed by a plateau till 210 °C. At this temperature, the band at 2040 cm^{-1} re-emerged, concomitant with a steep increase in the conversion.

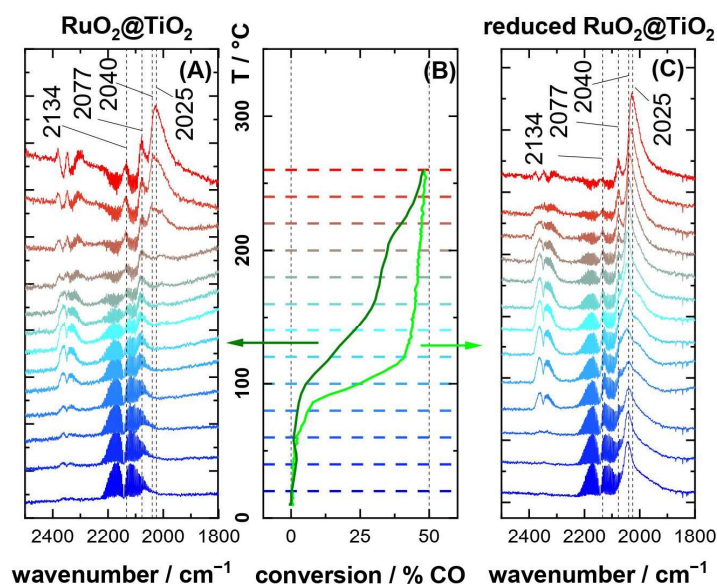


Figure 5. Operando DRIFT spectra of (A) $\text{RuO}_2@\text{TiO}_2$ and (C) reduced $\text{RuO}_2@\text{TiO}_2$, as well as (B) corresponding CO conversion data under reducing (1% O_2 /4% CO/95% Ar) reaction feed composition. For the conversion data, the dark green line corresponds to $\text{RuO}_2@\text{TiO}_2$ and the light green line to reduced $\text{RuO}_2@\text{TiO}_2$. The temperature axis of the conversion plot is marked by dashed lines in the color of the corresponding DRIFT spectra. Spectra are recorded in 20 °C increments. The heating ramp is 1.8 $\text{K}\cdot\text{min}^{-1}$.

With a further increase in the temperature, the 2040 cm^{-1} band diminished and merged with the 2025 cm^{-1} signal. At 260 °C, only bands at 2134 cm^{-1} , 2075 cm^{-1} , and 2025 cm^{-1} could be discerned clearly, with the latter being the most prominent one. Different from $\text{RuO}_2@\text{TiO}_2$ under oxidizing conditions, here a clear correlation between the partial reduction of the catalyst and an increase in activity was observed.

For DRIFTS of reduced $\text{RuO}_2@\text{TiO}_2$ under reducing reaction conditions (Figure 5C), the bands of adsorbed CO initially looked like those observed under oxidizing reaction conditions (Figure 3C). However, with increasing temperature, the high and low wavenumber shoulders of the 2040 cm^{-1} signal became more pronounced. Here, the 2040 cm^{-1} did not vanish above 100 °C. Instead, it remained clearly visible up to 200 °C, where it started to diminish. Note that for $\text{RuO}_2@\text{TiO}_2$ and reduced $\text{RuO}_2@\text{TiO}_2$ the spectra at 260 °C started to look very similar. The CO conversion of reduced $\text{RuO}_2@\text{TiO}_2$ under reducing conditions was markedly higher than that of $\text{RuO}_2@\text{TiO}_2$ throughout the entire temperature region.

Conversion plots and DRIFT spectra for a second heating ramp are summarized in Figure 6. The spectra were recorded after the catalyst was cooled back to room temperature. For both reducing and oxidizing reaction conditions, the DRIFT spectra looked similar regardless of the initial state of the catalyst. For reducing conditions, both samples exhibited bands at ca. 2135 cm^{-1} , 2060 cm^{-1} , and 2000 cm^{-1} , with almost identical shape and intensity (cf. Figure 6B, green spectra), which were characteristic for the partial reduction of the catalyst. For oxidizing conditions, the main band was 2077 cm^{-1} (cf. Figure 6B, blue spectra), but additionally, some weak signals were observed reaching down to 2000 cm^{-1} , as also seen in Figure 4. The conversion curves converged as well for the second heating ramp for all samples only depending on the gas feed composition. For reducing conditions,

the conversion curves (Figure 6A) were practically identical. The only difference with respect to the first heating ramp of reduced $\text{RuO}_2@\text{TiO}_2$ (shown in grey) is that the conversion was slightly lower throughout the temperature range and the conversion during the second heat-up of $\text{RuO}_2@\text{TiO}_2$ still exhibited hints of the high temperature conversion plateau.

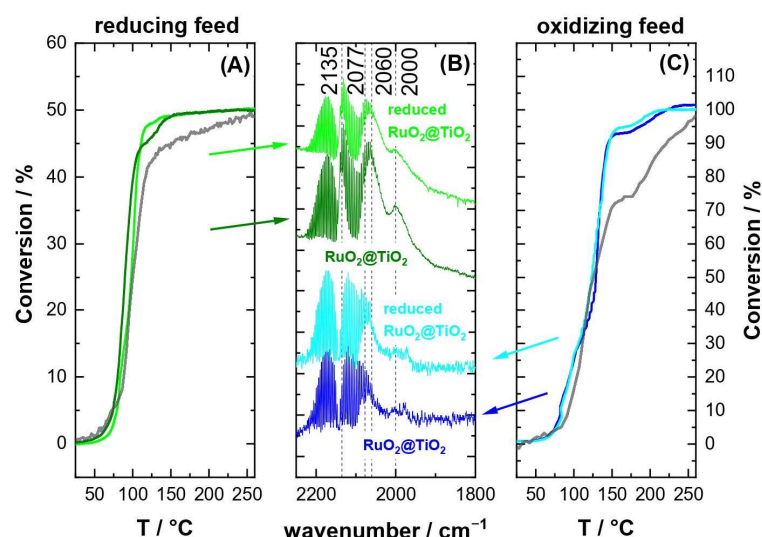


Figure 6. Operando DRIFT spectra and conversion of $\text{RuO}_2@\text{TiO}_2$ and reduced $\text{RuO}_2@\text{TiO}_2$ under (A) reducing and (C) oxidizing reaction feed composition for the second reaction heat-up. The spectra (B) are recorded after cooling the catalyst to room temperature. The grey conversion curves represent the conversion of the first heat-up for the $\text{RuO}_2@\text{TiO}_2$ and reduced $\text{RuO}_2@\text{TiO}_2$, as shown in Figures 3 and 5, respectively. Regardless of the initial state of the catalyst, spectra and conversion converged in accordance with the reaction feed.

For oxidizing conditions (Figure 6C), the differences in the conversion curves were more profound between the first and second heat ramps. The conversion plateau of the second heating ramp was markedly reduced relative to the first heat-up, signifying a clear correlation between activity and the presence of low wavenumber signals. However, the conversion curves for the second heat-up for both $\text{RuO}_2@\text{TiO}_2$ and reduced $\text{RuO}_2@\text{TiO}_2$ were practically identical and depended only on the reaction conditions. Overall, we can conclude from Figure 6 that the catalyst adapted dynamically to the same active phase regardless of whether it started from the oxidized or the reduced sample, but of course depending on the reaction environment.

3. Discussion

3.1. Stretching Vibrations of Adsorbed CO Probing the Actual Surface Oxidation State of RuO_2

Table 1 summarizes stretching modes of adsorbed CO for various Ru-based catalysts reported in the literature. We note that the assignment of the band positions to specific adsorption sites vary sometimes between different publications. This is likely due to exact band positions being dependent on many factors, such as coverage of CO and O, as well as the oxidation state of the adsorption site. A few general trends can, however, be identified. RuO_2 bands below 2000 cm^{-1} are assigned to CO on bridge positions, whereas those above 2000 cm^{-1} are ascribed to on-top CO. Here, a bridge position means CO being adsorbed to two adjacent Ru atoms, whereas on-top means CO on a single Ru atom. Infrared bands between 2000 and 2050 cm^{-1} were mainly observed for reduced RuO_2 or supposedly metallic samples. Note that Peden et al. [30], who assigned the band at 2040 cm^{-1} to metallic Ru, exposed the sample to strongly oxidizing conditions before the measurement.

Bands in the region of 2050–2100 cm^{-1} are assigned to both RuO_2 and metallic Ru. Bands above 2100 cm^{-1} are assigned to $\text{Ru}^{x+}(\text{CO})_y$, which is linked to partial reduction of RuO_2 or to CO on fully O covered $\text{RuO}_2(110)$ surfaces in some single-crystal studies.

Table 1. Vibrational band positions of CO on a Ru-based catalyst, as reported in the literature.

Band Position/ cm^{-1}	Adsorbed Species	Substrate	Ref.	Remarks
1860–1970	CO	Mildly reduced $\text{RuO}_2(110)$	[31]	Bridging CO being the majority species
2070–2080	CO	Mildly reduced $\text{RuO}_2(110)$	[31]	On-top and bridging CO couple to a single band
2000–2050	$[\text{Ru}^0\text{-CO}]$ -linear	$\text{Ru}/\text{Al}_2\text{O}_3$	[32]	Terminal CO
2010–2070	terminal CO	Ru-carbonyl	[33,34]	Depends on the carbonyl size
2048	CO	$\text{Ru}(001)$	[30]	Measured after exposure to oxidizing conditions; likely partially oxidized
2068	$(\text{CO}+\text{O})(2 \times 2)$	$\text{Ru}(001)$	[35]	--
2080	CO	$\text{Ru}(001)$	[30]	Measured under strongly oxidizing conditions at 500 K, likely oxidized
2100–2123	CO	Stoichiometric $\text{RuO}_2(110)$	[31]	On-top CO on stoichiometric $\text{RuO}_2(110)$
2100–2135	CO/O	$\text{RuO}_2(110)$	[36]	On-top CO being the majority species
2100–2150	CO/O	$\text{RuO}_2(110)$	[31]	O being the majority species; on-top CO embedded in O matrix
2070, 2130	$\text{Ru}^{x+}(\text{CO})_3$	$\text{Ru}/\text{Al}_2\text{O}_3$	[32,37]	$x = 1\text{--}3$
2134	$\text{Ru}^{x+}(\text{CO})_y$	Ru/SiO_2	[38]	Linked to oxidation of Ru
2135	$\text{Ru}^{x+}(\text{CO})_y$	Reduced $\text{RuO}_2(110)$	[3]	x and y undetermined; linked to surface roughening due to reduction

The CO adsorption on $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$ at 20 °C resulted in one distinct DRIFT signal at around 2060 cm^{-1} . Although the band position was slightly different between the two catalysts, it varied more substantially due to coverage effects and the occupancy of bridge positions by oxygen. Accordingly, this spectral feature alone was insufficient for characterization of the chemical state of the catalyst. It is quite surprising that only one single band was observed, as there are many different facets and adsorption sites expected to be present on the particle surfaces. The presence of only one symmetrical band in DRIFTS points toward efficient dipole–dipole coupling of the vibrational modes of all the different sites next to each other. This coupling was previously reported for RAIRS of CO on mildly reduced $\text{RuO}_2(110)$ [31].

When $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$ were exposed to a reducing reaction feed (1% O_2 /4% CO/95% Ar) at 300 °C, the samples were partially reduced and partially oxidized, respectively, as revealed in XP spectra (cf. Figure 1). This state of partial reduction of $\text{RuO}_2/\text{TiO}_2$ or partial oxidation of $\text{Ru}^0 + \text{TiO}_2$ was also corroborated by a dedicated DRIFTS signal at ca. 2000 cm^{-1} for both samples (cf. Figure 2). Additionally, a mid-wavenumber signal around 2040 cm^{-1} appeared for the reduced $\text{RuO}_2/\text{TiO}_2$ catalyst. This species was only visible as a shoulder in Figure 2B but, however, turned into an individual band when RuO_2 was reduced with 4% CO, as seen in the DRIFT spectra recorded at 20 °C in Figures 3C and 5C. Furthermore, a DRIFTS signal at 2135 cm^{-1} was discerned for reduced $\text{RuO}_2/\text{TiO}_2$, which can likely be attributed to a Ru-carbonyl species due to reduction induced roughening of the catalyst.

3.2. CO Oxidation as Case Study

The active phase of Ru-based catalysts in the CO oxidation reaction has been controversially debated over the last two decades. Broadly speaking, there are three interpretations of what constitutes the most active phase: (1) a metal surface with chemisorbed O reacting

with CO without oxidizing the Ru itself [15,39–41], (2) an oxide surface with CO binding to coordinatively unsaturated Ru sites (Ru_{cus}) and reacting with adjacent bridging oxygen [31,36,42–44], and (3) a sub-stoichiometric RuO_x or mixture of phases. We elaborate on these different views on the active phase in the following sections.

Various UHV studies reported either metal or oxide to be the most active phase. On the one hand, Goodman and coworkers claimed to have identified metallic Ru as the active phase. This determination conflicts, however, with studies demonstrating that at low O coverages oxygen binds too strongly and at high O coverages CO binds too weakly [3,16,45], rendering metallic Ru inactive according to the Sabatier principle. This view is supported by the experiments of Narloch et al. [46], wherein CO desorbed from a mixed CO-O phase on Ru(0001) without forming CO_2 . In addition, it is important to note that in the study of Gao et al. [3], no structural information of the active phase was provided except for post-reaction Auger electron spectroscopy (AES) (coverage of oxygen was found to be close to one monolayer). We note that AES characterization was carried out after heating the sample to desorb residual CO from the surface. This procedure may have reduced any potentially present surface oxide.

On the other hand, RuO_2 has been favored as the active phase in CO oxidation by various other studies [31,36,42–44]. Gao et al. argued that RuO_2 is not active in catalytic CO oxidation due to its high adsorption energy for CO, leading to poisoning by CO [3] and an expected reaction order of -1 in CO. Meanwhile, this conclusion was disproven by Martynova et al. [47], who determined the reaction orders for CO oxidation over $\text{RuO}_2(110)$ to be $+1$ for CO and zero for O_2 . A reaction order of $+1$ in CO is compatible with a previous study of Seitsonen et al. [48], who found not only strongly but also weakly adsorbed CO on $\text{RuO}_2(110)$.

So far, we have considered results for single-crystal surfaces without considering defects like steps or edges. On powder catalysts, the abundance of steps, edges, and corners may provide sites with more favorable adsorption energies for both O and CO, as demonstrated by Kim et al. [49] and Šljivančanin et al. [50]. The importance of defects for Ru-catalyzed CO oxidation has already been discussed by Gao et al.: Defects may overcome unfavorable adsorption energies of Ru(0001) [3].

Let us now discuss the third option of multiple phases in coexistence. One motive of such a multi-phase system, discussed in the literature and often linked to increased activity, consists of an ultrathin layer of RuO_2 or sub-stoichiometric RuO_x over Ru-metal [16,47,51–53]. Martynova et al. [47] demonstrated that the activity of Ru(0001) increased substantially when a surface oxide layer of 1–7 ML grew and that its activity was even higher when this surface oxide was disordered.

Another motive discussed in the literature is that of oxide and reduced oxides or even metallic phases coexisting on the surface [42,47,54,55]. Blume et al. [55] identified with XPS microscopy that oxidized RuO_2 and reduced RuO_x areas coexist on Ru(0001) during CO oxidation. They correlated the coexistence of both phases with increased activity. Martynova et al. [47] demonstrated that Ru(0001) formed a surface oxide in coexistence with an oxygen adsorption phase on Ru(0001) when exposed to 10^{-4} mbar O_2 at 300–400 °C and connected the increase in activity to an expansion of the oxide phase. Therefore, it seems unlikely that RuO_2 or Ru surfaces stay in their fully oxidic or metallic state, respectively, when exposed to reaction conditions.

Overall, it can be summarized that the presence of multiple phases of RuO_2 and Ru has been linked to higher activity of the catalyst. Some of these phases may only be present under reaction conditions or in small fractions. As such, they could easily be missed, especially in non-operando measurements. This may also explain the controversial discussion in the literature about the active phase of Ru/ RuO_2 in the CO oxidation. How multiple phases correlate to increased activity is, however, still unclear. According to the literature, it could be a core shell structure with a thin oxide layer on top of a metal core, a sub-stoichiometric RuO_x , or coexistence of these phases. In UHV studies, the reduction of $\text{RuO}_2(110)$ and $\text{RuO}_2(100)$ has shown to not lead to sub-stoichiometric RuO_x phases.

Instead, the RuO_2 decomposes into RuO_2 and Ru (with adsorbed oxygen) patches under reducing reaction conditions [56].

Due to the dynamic behavior of the catalyst (cf. also discussion of Figure 6) depending on the applied gas composition, it is paramount to conduct operando spectroscopic experiments with supported powder catalysts. In this study, we investigated RuO_2 supported on rutile TiO_2 in a flow reactor cell adapted to a DRIFTS spectrometer. We found that $\text{RuO}_2/\text{TiO}_2$ and reduced $\text{RuO}_2/\text{TiO}_2$ revealed significant differences in activity when exposed to various CO oxidation reaction conditions (cf. Figures 3B and 5B). Regardless of the CO oxidation reaction conditions being reducing or oxidizing, reduced $\text{RuO}_2/\text{TiO}_2$ turned out to be always significantly more active than $\text{RuO}_2/\text{TiO}_2$.

Under oxidizing conditions, both samples ($\text{RuO}_2/\text{TiO}_2$ and reduced $\text{RuO}_2/\text{TiO}_2$) were similarly active at low temperatures, but at 100 °C the conversion on reduced- $\text{RuO}_2/\text{TiO}_2$ increased steeply and remained higher than that of $\text{RuO}_2/\text{TiO}_2$. It is important to note that the conversion for $\text{RuO}_2/\text{TiO}_2$ reached a plateau from 150 °C up to 180 °C and then increased again. Taking into consideration that a chemical reduction of $\text{RuO}_2/\text{TiO}_2$ can occur even under oxidizing reaction conditions (cf. Figure 4), the increased conversion above 180 °C is correlated with the reduction of $\text{RuO}_2/\text{TiO}_2$. This interpretation is supported by the fact that 180 °C is also the temperature at which reduction of $\text{RuO}_2/\text{TiO}_2$ under reducing reaction conditions sets in (cf. Figure 5A).

The activity behavior of the samples was quite similar under reducing conditions. Above 60 °C, reduced $\text{RuO}_2/\text{TiO}_2$ revealed higher conversions than $\text{RuO}_2/\text{TiO}_2$ throughout the entire temperature range. Although the conversion of $\text{RuO}_2/\text{TiO}_2$ did not exhibit a plateau, it only increased slightly in the temperature region of 160–200 °C. In this temperature region, a slight reduction of $\text{RuO}_2/\text{TiO}_2$ was observed in DRIFTS. For even higher temperatures, DRIFT spectra evidenced pronounced reduction concomitantly with an increase in CO conversion, thus again correlating chemical reduction of $\text{RuO}_2/\text{TiO}_2$ with an increase in activity.

Gao et al. [3] proposed that the interaction between Ru metal and RuO_2 may play an important role in CO oxidation on RuO_2 . Farkas et al. [31,36] and Blume et al. [55] reported on a surface-phase separation into oxygen-rich and -depleted areas occurring on RuO_2 during CO oxidation, with the latter being the phase of enhanced activity. The increased activity of the partially reduced RuO_2 surface may even suggest bifunctionality such as that discussed for PdO. Weaver et al. [5] argued that on partially reduced PdO, CO oxidation is most favorable on the metal Pd surface, which is supplied with O from surrounding PdO. The bifunctionality of partially reduced RuO_2 would also be in line with the mechanistic arguments regarding too strong or too weak adsorption for CO and O on Ru and RuO_2 . Boundary regions may offer adsorption sites with intermediary adsorption energies, which would be favorable for CO oxidation, according to the Sabatier principle.

The adsorbed CO species resulting in the 2040 cm^{-1} band in DRIFTS seemed to be especially active. On the reduced catalyst, this species reacted off at ca. 100 °C under oxidizing conditions, leaving the high- and low-frequency bands in DRIFTS, which were consumed only above 200 °C (cf. Figure 3C). Under reducing conditions, the same species was observed in conjunction with an activity increase for $\text{RuO}_2/\text{TiO}_2$ at 200 °C; this CO species remained observable since excess CO was present in the gas phase. Under reducing conditions, the 2040 cm^{-1} band was preserved up to 220 °C on reduced $\text{RuO}_2/\text{TiO}_2$ in conjunction with the sample showing significantly higher activity than its oxidized counterpart (cf. Figure 5A,C). In both cases ($\text{RuO}_2/\text{TiO}_2$ and reduced- $\text{RuO}_2/\text{TiO}_2$), the band was consumed at temperatures above 220 °C. The fact that the 2040 cm^{-1} CO species was stable up to 200 °C under reducing conditions further corroborates that its disappearance at 100 °C under oxidizing conditions cannot have been due to desorption but actually was caused by a higher reactivity of this species. The reappearance of the 2040 cm^{-1} band when the samples were cooled under reducing conditions (Figure S4) demonstrates that the corresponding sites remained present on the catalyst. A possible assignment of this band is that of CO adsorbed in the boundary regions between surface phases, most likely

metallic Ru (with adsorbed O) and RuO₂. This would also explain the absence of this band on partially oxidized Ru⁰ + TiO₂ (cf. Figure 2B), as here no RuO₂ may be present.

An interesting observation about the low wavenumber band is its variable position (between 1985 cm^{−1} and 2010 cm^{−1}) and asymmetric shape, whereas the position of the other bands in DRIFTS remained largely constant. This suggests that this band comprised CO species at various adsorption sites whose contributions changed depending on the chemical state of the catalyst. This interpretation would be in line with a varying composition of reduced RuO₂, as it is further reduced or re-oxidized. This behavior was especially apparent for reduced RuO₂@TiO₂ under oxidizing conditions between 120 and 180 °C. Here, the low wavenumber band shifted to higher wavenumbers and became more symmetric with higher reaction temperature (cf. Figure 3C) as the surface oxidized and approached the fully oxidized RuO₂.

Based on this discussion, we propose the following assignment of bands for partially reduced RuO₂ under CO oxidation conditions:

- I. 1985–2030 cm^{−1}: CO on partially reduced RuO₂ with shape and position changing according to surface composition
- II. 2040 cm^{−1}: CO sitting possibly in boundary region between surface phases with the highest activity.
- III. 2075 cm^{−1}: CO on oxide RuO₂
- IV. 2135 cm^{−1}: carbonyl Ru^{x+}(CO)_y, which can form on highly under-coordinated Ru^{x+} sites. Reduced RuO₂ has been demonstrated to roughen [54,56], which would provide such under-coordinated Ru^{x+} at the edges and corners [3].

Actually, very similar bands were reported by Gao et al. [3] when exposing Ru(0001) and RuO₂(110) to oxidizing and reducing reaction conditions, respectively, at 50 Torr and 500 K. For Ru(0001) under oxidizing conditions (O₂/CO = 5/1), at first no bands were observed; after 1–1.5 h bands at 2130, 2080, and 2040 cm^{−1} appeared; and finally, after 2.5 h a single band at 2080 cm^{−1} remained. This experiment is consistent with the surface going through partial oxidation and finally arriving at an oxide surface, according to our interpretation of the bands. Conversely, for RuO₂(110) under reducing conditions (O₂/CO = 1/10) the 2080 cm^{−1} band was dominant at first. After 5 min of reduction the RAIR spectrum showed a weak low wavenumber shoulder and the 2130 cm^{−1} band. During the next 6 h of reaction time, bands at 2050 and 2020 cm^{−1} increased in intensity with the 2080 cm^{−1} band diminishing. Altogether, these RAIRS data [3] on single-crystalline surfaces of Ru/RuO₂ are in reasonable agreement with our DRIFTS experiments of Ru-based powder catalysts supported on rutile TiO₂.

4. Experimental Details

4.1. Sample Preparation and Characterization

For DRIFTS experiments, we prepared RuO₂ supported on rutile TiO₂ (RuO₂@TiO₂) by a modified Pechini synthesis, as described in detail by Khalid et al. [57]. This ensured an even dispersion of the catalytically active oxides, which absorb IR radiation, on the reflective TiO₂ matrix. The BET surface area of the used support was 20 m²·g^{−1}, with a mean particle size of 100 nm. Another advantage of this type of preparation is the better comparability of DRIFTS results with the kinetic data of previous work. The RuO₂@TiO₂ samples were thoroughly characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and Raman spectroscopy in a previous study [57].

Two types of samples studied were oxidized and reduced samples of 2 mol% supported RuO₂. Two mol% RuO₂ on 20 m²/g TiO₂ corresponds to an average thickness of 0.24 nm. Since RuO₂ is known to grow on TiO₂ with a thickness of no less than 3 monolayers or 1.5 nm [58], this corresponds to a surface coverage of maximally 16%. The samples obtained from the Pechini synthesis were first thermally oxidized or reduced by applying O₂ or CO at 300 °C. Although the supported RuO₂ could not be identified definitively by TEM micrographs, they showed no morphological differences between the oxidized and reduced samples (cf. Figure S5). These samples are referred to as RuO₂@TiO₂ and reduced

$\text{RuO}_2/\text{TiO}_2$, respectively, and are characterized by X-ray photoelectron spectroscopy (XPS). For XPS analysis, a PHI VersaProbe II instrument was used. The data were recorded employing a photon energy of 1486.6 eV (Al $K\alpha$ line).

DRIFT spectra of purely metallic Ru and purely oxidic RuO_2 samples were employed as references to assign the DRIFTS CO bands of $\text{RuO}_2/\text{TiO}_2$ under reaction conditions. Full reduction of our RuO_2 samples did not seem to be possible, as can be seen in Figure S1. To obtain the CO adsorption signals of pure metallic samples, we therefore used 33 w% of commercially available Ru (chempur) metal powder mixed with TiO_2 . These samples were also reductively pretreated to remove any surface oxides that may have formed by applying 4% CO at 300 °C for 4 h. This sample is referred to as $\text{Ru}^0 + \text{TiO}_2$. After this treatment, XPS indicated pure metallic samples, as demonstrated in Figure 1.

Figure 1 also depicts XP spectra of $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$ after being exposed to a reducing reaction feed (4% CO/1% O_2 /95% Ar) at 300 °C. Quite surprisingly, the spectra of $\text{RuO}_2/\text{TiO}_2$ and $\text{Ru}^0 + \text{TiO}_2$ exhibited both oxide and metal Ru signals. The samples were therefore in a state of partial reduction/oxidation.

4.2. Reaction Conditions

The reactor setup was built in house, and the description of it can be found in a recent publication by our group [10]. It consists of a gas supply controlled by mass flow controllers, a custom designed reactor cell made from 1.4742 Ni-free steel, and a mass spectrometer for gas analysis. To derive the conversion from MS data, the CO_2 signal ($m/z = 44$) was normalized by its maximum value (at full conversion). Full consumption of O_2 (for reducing conditions) or CO (for oxidizing conditions) was used to determine the point at which full conversion was achieved. For oxidizing conditions, some CO always remained in the MS spectrum due to the cracking pattern of CO_2 . In this case, full conversion was assumed when no further decrease in $m/z = 28$ and no further increase in $m/z = 44$ was observed with rising temperature.

Total flow for all experiments was 50 sccm, whereas the heating ramp was set as $1.8 \text{ K} \cdot \text{min}^{-1}$. The gas compositions for the various experiments are compiled in Table 2. In order to minimize temperature changes induced by the reaction heat, by keeping the concentration of the reactants as small as possible, as well as due to limitations in the MFC flow range, the ratio of reactive gas to carrier gas had to be varied.

Table 2. Gas compositions for different experiments.

Reaction Conditions	Ar/%	O_2 /%	CO/%
Oxidizing	96	2	2
Reducing	95	1	4
CO only	96	-	4

5. Conclusions

CO was employed as a probe molecule to study the actual oxidation state of a supported $\text{RuO}_2/\text{TiO}_2$ catalyst during the CO oxidation reaction. To do so, online mass spectrometry (MS) was coupled with operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The CO DRIFT spectra of the pure oxide $\text{RuO}_2/\text{TiO}_2$ samples and the pure metal $\text{Ru}^0 + \text{TiO}_2$ were governed by a single mode at ca. 2060 cm^{-1} . Partially reduced $\text{RuO}_2/\text{TiO}_2$, on the other hand, was characterized by four distinct band regions in DRIFTS at 2135, 2075, 2040, and 2000 cm^{-1} . The combination of conversion (MS) and vibrational CO data (DRIFTS) revealed higher activity of reduced- $\text{RuO}_2/\text{TiO}_2$ than its oxidized counterpart both under reducing and oxidizing CO oxidation reaction conditions. The catalysts were shown to adopt the catalytically active phase dynamically to the reaction conditions independent of their initial state, only depending on the applied reaction mixture. Most surprisingly, even under oxidizing reaction conditions partial reduction of

RuO₂@TiO₂ was encountered. The CO species at 2040 cm^{−1} in DRIFTS was shown to be especially reactive.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal13081178/s1>, Table S1: XPS fit parameter; Figure S1: Ru 3d XP spectra of oxidized and reduced RuO₂; Figure S2: DRIFTS spectrum of CO adsorption on Ru⁰+TiO₂, which has after oxidative pretreatment under 4% O₂ at 300 °C for 12h; Figure S3: IR spectra of pre-oxidized TiO₂ heated in a CO atmosphere; Figure S4: Operando DRIFT spectra of reduced-RuO₂@TiO₂ during cool down under reducing (1% O₂/4% CO/95% Ar) reaction feed composition; Figure S5: TEM micrographs of RuO₂@TiO₂ (left) before and (right) after reduction.

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4.2 Publication II: Operando CO Infrared Spectroscopy and On-Line Mass Spectrometry for Studying the Active Phase of IrO₂ in the Catalytic CO Oxidation Reaction

This publication is on identifying the most active phase of IrO₂ in the catalytic oxidation of CO. Here, CO was used as a probe molecule for the oxidation state of the catalyst during reaction conditions using operando DRIFTS. As a benchmark metallic Ir⁰ mixed with TiO₂ and fully oxidized IrO₂ supported on TiO₂ were subjected to CO-containing gas feeds. DRIFT spectra recorded under these conditions reveal singular symmetric CO adsorption bands in the region of 2087-2060 cm⁻¹ on both materials. This demonstrates that a clear distinction of purely metallic or oxidic Ir-surfaces is not possible, due likely to dipole-dipole coupling of the adsorbed CO molecules. Partially reducing the IrO₂ or partially oxidizing the Ir⁰ samples results in a characteristic broad asymmetric band in DRIFTS with its highest intensity at 2085 cm⁻¹ and a broad shoulder reaching down to 1800 cm⁻¹. This characteristic signal is subsequently used to identify whether the IrO₂ catalyst is in a partially reduced state under reaction conditions. Partially reduced and fully oxidized IrO₂ were exposed to reducing and oxidizing CO oxidation reaction conditions. By correlating the characteristic bands in DRIFT spectra and conversion recorded by MS it is demonstrated that partially reduced IrO₂ exhibits a higher activity under both reaction conditions.

H. Over and I devised the experimental schedule. T. Weber and L. Glatthaar performed the XPS measurements. I prepared the samples and performed the DRIFTS experiments. H. Over, and I contributed through scientific discussions of the data. H. Over and I wrote the draft version of the manuscript. All authors revised the manuscript and have given approval to the final version.

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Article

Operando CO Infrared Spectroscopy and On-Line Mass Spectrometry for Studying the Active Phase of IrO₂ in the Catalytic CO Oxidation Reaction

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Abstract: We combine operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) with on-line mass spectrometry (MS) to study the correlation between the oxidation state of titania-supported IrO₂ catalysts (IrO₂@TiO₂) and their catalytic activity in the prototypical CO oxidation reaction. Here, the stretching vibration of adsorbed CO_{ad} serves as the probe. DRIFTS provides information on both surface and gas phase species. Partially reduced IrO₂ is shown to be significantly more active than its fully oxidized counterpart, with onset and full conversion temperatures being about 50 °C lower for reduced IrO₂. By operando DRIFTS, this increase in activity is traced to a partially reduced state of the catalysts, as evidenced by a broad IR band of adsorbed CO reaching from 2080 to 1800 cm⁻¹.

Keywords: IrO₂ supported on rutile TiO₂; catalytic CO oxidation; catalytically active phase; operando DRIFTS; on-line mass spectrometry



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1. Introduction

The controversial discussion over whether the (late) transition metal or its oxide constitutes the active phase in a catalytic oxidation reaction such as CO or methane oxidation is still ongoing and not yet settled. The most prominent catalytic systems where this fundamental question has been risen include ruthenium [1,2], palladium [3], iridium [4], and platinum [5]. Since the catalyst may dynamically adapt its chemical composition and structure to the actual reaction mixture [6], operando characterization methods are mandatory in catalysis research to study the catalytically active phase and to unveil potential reaction intermediates on the catalyst's surface [7,8].

Infrared (IR) spectroscopy has been demonstrated to be a powerful technique in catalysis research for identifying reaction intermediates at the catalysts' surface [9]. Employing a probe molecule, such as CO, infrared spectroscopy can also be used to probe the status and chemical nature of the active phase of the catalyst [10,11]. There are several benefits of using CO as a probe molecule in infrared spectroscopy [12,13], most notably the large cross section of CO for IR absorption and the convenient frequency range of around 2000 cm⁻¹. The actual stretching frequency of the adsorbed CO depends sensitively on many parameters, including the adsorption site (coordination of CO), the local chemical environment, the coverage of CO, the occupation of d-orbitals of the active component, the oxidation state of the coordinated metal ions, and the electric field at the surface [14]. This renders CO a versatile probe molecule to explore the properties of the catalyst's surface.

Reducible oxides [15] are particularly prone to reaction-induced changes in that they can transform between the metallic and the oxide phase depending on the specific reaction conditions. Here, we consider IrO₂ supported on rutile TiO₂, which has revealed high activity in the combustion of methane [16,17], propane [18], and CO [19,20]. How-

ever, even more important than in thermal catalysis may be the use of these materials in electrocatalysis, including the chlorine and oxygen evolution reaction [21–25].

In this report, diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) [26,27] is employed to elucidate the active phase of $\text{IrO}_2@\text{TiO}_2$ by utilizing CO as a probe molecule. In doing so, we first prepare fully oxidized and fully reduced catalysts whose DRIFT spectra serve as reference spectra for the subsequent interpretation of operando CO spectra acquired during CO oxidation - a well-documented model reaction for oxidation catalysis [28] - under various reaction conditions. It turns out that the partially reduced $\text{IrO}_2@\text{TiO}_2$ catalyst constitutes the most active catalyst in the CO oxidation reaction, regardless of whether the reaction takes place under reducing or oxidizing reaction conditions.

2. Experimental Details

2.1. In Situ DRIFTS Cell

For the present study we constructed a new high-pressure reactor setup that is integrated into an in situ diffuse reflectance infrared Fourier transform spectrometer (spectrometer: Bruker Vertex 70v Sample; sample chamber module: Pike DiffIR) and connected to a mass spectrometer, as depicted in Figure 1.

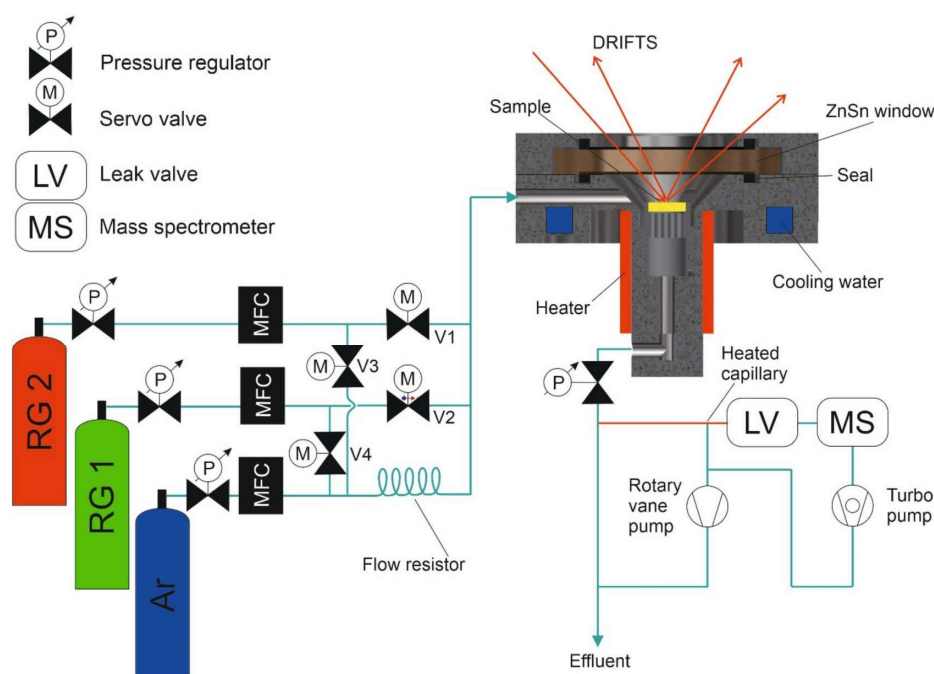


Figure 1. Scheme of the reactor setup with gas supply and analytics. The green lines represent steel tubes. The red arrows show the IR light striking the sample. Reactive gases are denoted as RG 1 and RG 2. The outer dimensions of the reactor cell are 55 mm in diameter and height. The catalyst bed (yellow) is 7 mm in diameter and 3 mm high.

The DRIFTS apparatus comprises four sections: gas supply, reactor cell, optics, and gas analytics. In the gas supply part (left side of Figure 1), the gas bottles are attached to mass flow controllers (MFCs) through pressure regulators. The MFCs are connected to a network of tubes and servo valves, which are used to flush the gas supply lines when switching gases during a measurement. While a reactive gas (RG) is in use, the respective horizontal shut-off valve (V1/V2) is open and the corresponding vertical flush valve (V3/V4) is closed. In this way the carrier gas goes through the flow resistor and mixes with the reactive gas at the T-junction. If a reactive gas is to be shut off, first the MFC is closed and subsequently the

flush valve is opened. Due to the flow resistance, the carrier gas now mainly flows through the RG line, removing any residual reactive gas. After 15 s, both the horizontal (V1/V2) and the vertical (V3/V4) valves are closed and the reactor can resume normal operation. Without this flush system, purging the reactive gas line to below the mass spectrometer (MS) detection limit can take up to 2 h.

The reactor cell itself is made from 1.4742 Ni-free steel, as Ni-containing steel itself is a CO oxidation catalyst and readily forms Ni carbonyls that can be deposited on the catalyst bed, thus affecting its activity. If CO is used as the reactant, a nickel carbonyl trap consisting of heated copper tubing is connected between the gas bottle and the MFC. The cell is designed in a way that the dead volume is minimized, facilitating rapid gas exchange. The cell consists of a conical chamber and three gas inlets separated by 120° from each other. On top of the chamber, a ZnSe window is tightened with a metal ring and Viton seals. At the bottom of the cell, the sample cup is screwed into the shaft. On the outside of this shaft, a 300 W heater is placed. To protect the seals and window from high temperatures, the outer part of the cell has a channel connected to a water cooling system. The gas outlet is located at the lower end of the shaft, behind which an overpressure valve can be placed, enabling pressurization of the reactor up to 20 bar.

The path of the IR light from the spectrometer as well as the temperature measurement via pyrometer (B+B DM501) are illustrated in Figure S1. The pyrometer measures the temperature of the sample through the intensity of thermal radiation with a wavenumber around 4350 cm^{-1} . To ensure accurate measurements, no light from the globar should reach the pyrometer. This is accomplished by a long-pass filter behind the globar and a short-pass filter in front of the pyrometer, both with an absorption edge at 4350 cm^{-1} . The pyrometer is calibrated by heating the sample in the reactor with a thermocouple placed inside the catalyst bed. To make sure that the thermal radiation of the sample does not overload the mercury cadmium telluride detector, an iris aperture and a band-pass filter are placed in front of it. At the exit of the reactor cell, the effluent gas is analyzed by a quadrupole mass spectrometer (QMS, Pfeiffer QMG220). The transfer of some of the effluent stream to a T-junction is achieved by a heated steel capillary, which is evacuated by a rotary vane pump, enabling a quick gas exchange in the junction. Also attached to this junction is a leak valve that allows the introduction of a minor portion of the effluent gas to a UHV system containing the QMS. The time delay of the MS signal and the MFC gas flow is indicated in Figure S2. When the MFC gas flow is switched on, a short spike in flow is created due to the pressure build-up behind the servo valve (compare Figure S2). After 45 s, a steady state is reached in the MS signal. When the gas is switched off and flushed, it takes 40 s for all gases to be removed from the system, reaching the background intensity of the MS signal. The conversion is calculated by normalizing the CO_2 signal ($m/z = 44$) by its maximum value (at full conversion). The point of full conversion is determined by the full consumption of O_2 (for reducing conditions) or CO (for oxidizing conditions). In the latter case, some CO will always remain in the MS spectrum, due to the cracking pattern of CO_2 . Here, full conversion is assumed, when no further decrease in $m/z = 28$ and no further increase in $m/z = 44$ is observed with increasing temperature.

Details on the data treatment of the DRIFT spectra can be found under Figure S3.

2.2. Sample Preparation and Characterization

In DRIFTS experiments, samples with high absorbance in the investigated spectral range are commonly mixed with a reflective powder matrix. Similar to dilution in the IR spectroscopy of solutions, this serves the purpose that the light, scattered in the powder bed, has a shorter path through the absorbing medium before being reflected back. However, when mixing two powders, agglomerates of the respective components remain in the mixture. Harsh mixing methods like ball milling might reduce the amount of agglomerates, but bear the possibility of changing the sample by mechanochemistry. If light enters such an agglomerate it will likely be absorbed inside the agglomerate. To overcome this issue, we decided to prepare IrO_2 supported on rutile TiO_2 by a modified Pechini synthesis, as

described by Khalid et al. [16]. The samples used here were prepared with a lower loading of 2 mol%, as higher loadings are not reflective enough for DRIFTS measurements. Pechini constitutes a variant of sol–gel synthesis. Here, the metal ions are dissolved in water. In our case, IrCl_4 hydrate, purchased from fluorochem, was used. After complete dissolution the rutile TiO_2 support (particle size <100 nm), purchased from Sigma Aldrich (St. Louis, MO, USA), was added. The use of rutile TiO_2 ensures a high dispersion of rutile IrO_2 as indicated by previous studies [16,29,30]. Then a 100-times stoichiometric excess of citric acid, relative to the metal ions, is added to form a chelate complex of the metal ions and the citric acid. This solution is heated to 60°C for 30 min to ensure complete dissolution and complexation. Afterward, three times the molar amount (relative to citric acid) of ethylene glycol is added. The resulting solution is then heated with maximum heating power to induce polymericization/polycondensation. Here, the carboxylic acid groups of the citric acid/metal ion complexes and the alcohol groups of the ethylene glycol form ester bonds, resulting in a 3D carbon network. In this network, the rutile TiO_2 particles are trapped and surrounded by metal ion complexes. Heating is continued until the solvent evaporates, after which the resulting gel is calcined at 450°C for 7 h in air. During calcination the metal ions can nucleate directly on the rutile TiO_2 . This preparation ensures a homogeneous dispersion of the IR absorbing, catalytically active oxides on the reflective TiO_2 matrix. Similar samples were thoroughly characterized by Raman spectroscopy, X-ray diffraction (XRD), and transmission electron microscopy (TEM) by Khalid et al. [16] Due to the lower loadings employed in this study, Raman spectroscopy and XRD could not be carried out on the specific samples used here. The reason for this is that the detection limits of these techniques are too low and/or the signals of IrO_2 are overshadowed by TiO_2 . TEM images of the pure TiO_2 support and 2 mol% supported IrO_2 on TiO_2 are shown in Figure S4.

The 2 mol% supported IrO_2 on TiO_2 samples obtained from the Pechini synthesis were first thermally oxidized or reduced by exposing the sample to 4% O_2 or to 4% CO at 300°C , respectively. These samples are referred to as $\text{IrO}_2@\text{TiO}_2$ or reduced $\text{IrO}_2@\text{TiO}_2$. To assign the DRIFTS CO bands of $\text{IrO}_2@\text{TiO}_2$ under reaction conditions, it is necessary to compare them with reference DRIFT spectra of purely metallic Ir and purely oxidic IrO_2 samples.

When used to prepare high loadings, the Pechini synthesis tends to produce oxide particles with a metal core [31–34]. This is due to the reducing effect of the carbon matrix in the gel on the particles formed in the early stages of calcination. This effect, however, diminishes when preparing small loadings like the 2 mol% IrO_2 employed in this work. Most likely, the first particles form later in the calcination process when the metal ion concentration is lower. Therefore, pure IrO_2 supported on rutile TiO_2 can be prepared by the Pechini synthesis approach, as evidenced by the X-ray photoelectron spectroscopy (XPS) data depicted in Figure 2A. For the XPS characterization, a PHI VersaProbe IV instrument is employed. The measurements are conducted with a photon energy of 1486.6 eV ($\text{Al K}\alpha$ line).

Quite in contrast, the full reduction of $\text{IrO}_2@\text{TiO}_2$ to metallic Ir does not seem to be possible, as can be seen in Figure S5. Therefore, 33 w% of commercially available Ir metal powder (abcr GmbH) was physically mixed with TiO_2 as a matrix to collect CO adsorption signals of pure metallic samples (these samples are referred to as $\text{Ir}^0 + \text{TiO}_2$). After reductive pretreatment for 4 h at 300°C under 4% CO , the XPS indicates pure Ir metal (cf. Figure 2C) without any traces of IrO_2 -related spectral features.

Figure 2B,D show XP spectra of $\text{Ir}^0 + \text{TiO}_2$ and $\text{IrO}_2@\text{TiO}_2$ after being exposed to reducing CO oxidation conditions (1% O_2 /4% CO /95% Ar) at 300°C . Here, the XP spectra show metal and oxide signals for $\text{Ir}^0 + \text{TiO}_2$ und $\text{IrO}_2@\text{TiO}_2$, thus evidencing a partially oxidized and reduced state, respectively. Raman spectra of Ir^0 before and after the same pretreatment (Figure S6) indicate clear signatures of IrO_2 .

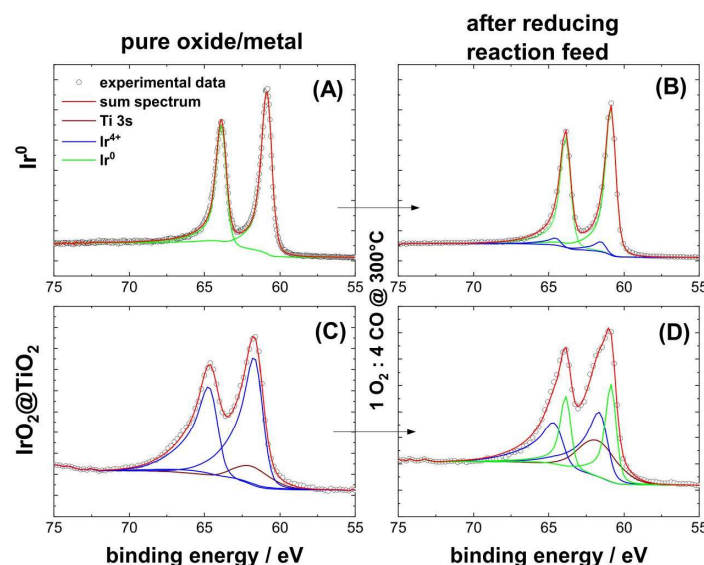


Figure 2. Ir 4f XPS spectra of (A) Ir^0 as well as (C) $\text{IrO}_2/\text{TiO}_2$. The latter sample is measured without TiO_2 , as otherwise the spectra were dominated by the Ti 3s feature. (B,D) show the respective samples after being exposed to reducing CO oxidation conditions (1% O_2 /4% CO/95% Ar) at 300 °C. The fit parameters for decomposition of the experimental spectra (circles) are provided in Table S1 of the Supplementary Materials.

2.3. Reaction Conditions

All experiments are conducted under a total flow of 50 sccm and a heating ramp of $1.8 \text{ K} \cdot \text{min}^{-1}$. The gas compositions for the various reaction conditions are compiled in Table 1.

Table 1. Gas compositions for different experiments.

Reaction Conditions	Ar/%	O_2 /%	CO/%
Oxidizing	96	2	2
Reducing	95	1	4
CO only	96	-	4

The ratio of reactive gas to carrier gas had to be varied during the CO oxidation case study, due to limitations in the MFC minimum flow and trying to keep concentration of the reactants as small as possible in order to minimize temperature variations induced by the heat of reaction.

3. Experimental Results

3.1. Characterization of Pre-Oxidized and Pre-Reduced $\text{IrO}_2/\text{TiO}_2$ and $\text{Ir}^0 + \text{TiO}_2$ Samples

The XP spectra in the Ir 4f binding energy region of the $\text{IrO}_2/\text{TiO}_2$ and $\text{Ir}^0 + \text{TiO}_2$ samples are summarized in Figure 2A,C. The fit parameters used can be found in the literature [35–38] and in Table S1. According to the Ir 4f spectrum in Figure 2C, iridium is fully oxidized in the case of $\text{IrO}_2/\text{TiO}_2$. Additionally, the spectrum shows a small signal of Ti 3s stemming from the TiO_2 support. Attempts to reduce $\text{IrO}_2/\text{TiO}_2$ are made, with the harshest reduction conditions being 4% H_2 at 600 °C for 24 h. It is, however, not possible to produce pure metallic particles, as shown by the XP spectra in Figure S5. The spectra of the mixture of $\text{Ir}^0 + \text{TiO}_2$ are dominated by the Ti 3s signal so heavily that

a meaningful deconvolution is not possible, therefore the pure Ir^0 powder was used instead for XPS analysis. Here the Ir 4f XP spectrum shows pure metallic Ir^0 . Under reducing CO oxidation conditions (1% O_2 /4% CO/95% Ar), the XP spectra of $\text{Ir}^0 + \text{TiO}_2$ and $\text{IrO}_2@ \text{TiO}_2$ in Figure 2B,D, respectively, indicate spectral features of both metallic and oxidic Ir. For $\text{Ir}^0 + \text{TiO}_2$ this effect seems to be less pronounced than for $\text{IrO}_2@ \text{TiO}_2$, which is likely due to the large size of the Ir^0 particles that can only be oxidized at the surface, so that the XPS signal is dominated by the bulk metal signal.

3.2. CO DRIFTS Experiments of Oxidized and Reduced $\text{IrO}_2@ \text{TiO}_2$ and $\text{Ir}^0 + \text{TiO}_2$ Samples

Figure 3A shows the CO DRIFT spectra of $\text{IrO}_2@ \text{TiO}_2$ and $\text{Ir}^0 + \text{TiO}_2$. As the samples consist of pure IrO_2 and pure metal Ir^0 , as demonstrated by the XPS, the DRIFT data serve as benchmark spectra to firmly assign characteristic spectral features of the DRIFT spectra during the CO oxidation. Here, only one distinct signal at 2060 cm^{-1} and 2087 cm^{-1} is revealed for $\text{IrO}_2@ \text{TiO}_2$ and $\text{Ir}^0 + \text{TiO}_2$, respectively. However, the band position of $\text{IrO}_2@ \text{TiO}_2$ at 2060 cm^{-1} varies under reaction conditions slightly with the temperature (cf. Figure 4A). As such, the oxidation state of the catalyst cannot unambiguously be derived from band position in DRIFTS alone.

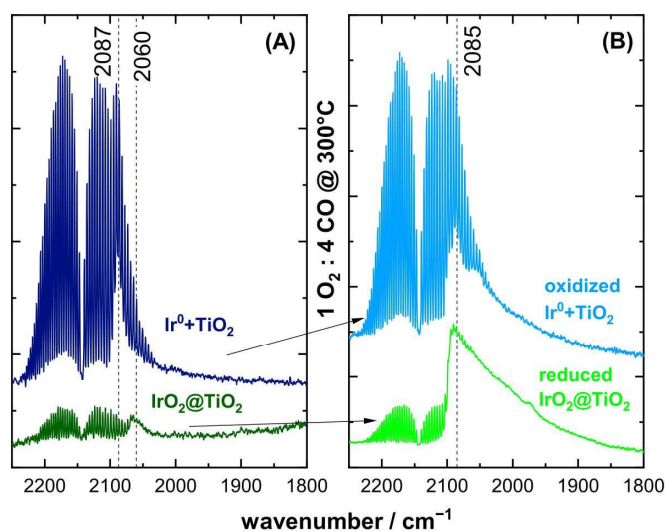


Figure 3. CO DRIFT spectra are shown for (A) commercial $\text{Ir}^0 + \text{TiO}_2$ in the purely metallic state of Ir as well as on $\text{IrO}_2@ \text{TiO}_2$ as prepared by the Pechini synthesis in the purely oxidic state of Ir on the left. In (B), similar spectra are shown for the same samples after being exposed to reducing CO oxidation conditions (1% O_2 /4% CO/95% Ar) at 300°C . All spectra are recorded at room temperature.

Under reaction conditions, the oxidation state of a catalyst may change dynamically when varying the temperature or the feed composition. It is therefore of particular interest to investigate the catalyst in an intermediary state of partial reduction/oxidation. In order to achieve this, the samples are exposed to a reducing CO oxidation mixture (1% O_2 /4% CO/95% Ar) at 300°C . Under this reaction condition, $\text{Ir}^0 + \text{TiO}_2$ is able to partially oxidize, while $\text{IrO}_2@ \text{TiO}_2$ may partially reduce, thus forming an intermediate phase for both catalysts. The DRIFT spectra of the samples after cooling to room temperature under reaction conditions are depicted in Figure 3B. Here, both samples show a major absorption band at 2085 cm^{-1} with a very broad shoulder reaching down to 1800 cm^{-1} . Some minor differences in the peak shape can be observed, like additional shoulder peaks at around 2060 cm^{-1} and slightly above 2085 cm^{-1} for the oxidized $\text{Ir}^0 + \text{TiO}_2$. The overall characteristic shape of the DRIFT spectra for both samples is, however, very similar and is

indicative of a unique intermediate phase that is formed by the partial reduction of IrO_2 and partial oxidation of Ir^0 .

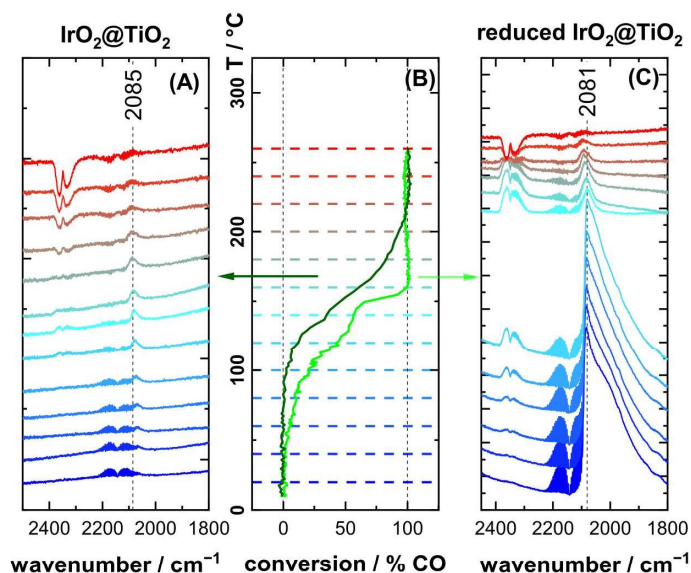


Figure 4. Operando DRIFT spectra of (A) $\text{IrO}_2@\text{TiO}_2$ and (C) reduced $\text{IrO}_2@\text{TiO}_2$, as well as (B) corresponding CO conversion data as measured by MS for oxidizing (2% O_2 /2% CO /96% Ar) reaction feed composition. For the MS data, the dark green line corresponds to $\text{IrO}_2@\text{TiO}_2$, and the light green line to reduced $\text{IrO}_2@\text{TiO}_2$. The temperature axis of MS and the color code of the dashed lines signify the temperatures of the DRIFT spectra. The temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 $\text{K}\cdot\text{min}^{-1}$.

Blank spectra are provided in Figure S7 for the rutile TiO_2 support alone without the active component. Here, no CO adsorption is discernible. A CO DRIFT spectrum of $\text{Ir}^0 + \text{TiO}_2$, having undergone oxidative pretreatment with 4% O_2 at 300 °C, is shown in Figure S8. As for $\text{IrO}_2@\text{TiO}_2$, only a single band without a broad shoulder is observed, indicating that the surface of $\text{Ir}^0 + \text{TiO}_2$ can form a surface oxide similar to that of $\text{IrO}_2@\text{TiO}_2$.

3.3. CO Oxidation Experiments of $\text{IrO}_2@\text{TiO}_2$ Samples

Figure 4 depicts the DRIFT spectra of $\text{IrO}_2@\text{TiO}_2$ and reduced $\text{IrO}_2@\text{TiO}_2$ during CO oxidation reaction under oxidizing conditions (2% O_2 /2% CO /96% Ar) at various temperatures, together with the corresponding CO conversion. Conversion data were produced by normalizing mass spectrometer (MS) data to their respective maxima, corresponding to the full conversion of CO.

For $\text{IrO}_2@\text{TiO}_2$, a single band appears at 2085 cm^{-1} (Figure 4A), as also observed in Figure 3A. This band remains unchanged in position and shape till it starts to diminish between 160 °C and 240 °C, while the reaction rate (MS) concomitantly increases. No further CO adsorption signals can be detected in DRIFTS above 240 °C. The CO conversion starts at around 100–120 °C as indicated by MS (Figure 4B) and the appearance of the CO_2 gas phase signal in DRIFTS starts at around 2350 cm^{-1} . As the temperature increases, heated gases (here CO and CO_2) in and directly above the catalyst layer start to emit IR radiation themselves. This causes the gas phase signals in the IR spectra to flip around 180–220 °C and look like “negative absorption”.

On reduced $\text{IrO}_2@\text{TiO}_2$, the dominant absorption band is again at 2080 cm^{-1} with a broad shoulder reaching down to 1800 cm^{-1} (Figure 4C). Here, the MS and CO_2 gas phase signal in DRIFTS show a significantly earlier onset of activity at ca. 50 °C, which

is about 50 °C lower in temperature than observed for the CO oxidation on IrO₂@TiO₂. Furthermore, MS shows higher activity of the reduced IrO₂@TiO₂ compared to IrO₂@TiO₂ throughout the entire temperature range, until IrO₂@TiO₂ reaches full conversion at 220 °C. A steep increase in activity is evident for the reduced IrO₂@TiO₂ in the temperature range from 140 °C to 160 °C, while full conversion is reached at 160 °C. This steep increase in activity is correlated with a pronounced change in the DRIFT spectra, where CO from the broad band is consumed leaving the previously observed single band at 2081 cm⁻¹. This band then slowly diminishes with increasing temperature until at 260 °C no surface CO signal is observable in DRIFTS.

Figure 5 shows the DRIFT spectra of reduced IrO₂@TiO₂ under oxidizing conditions during the cool down from 160 °C. Before those spectra are recorded, the sample is heated to 160 °C, so the broad shoulder is consumed as previously seen in Figure 4C.

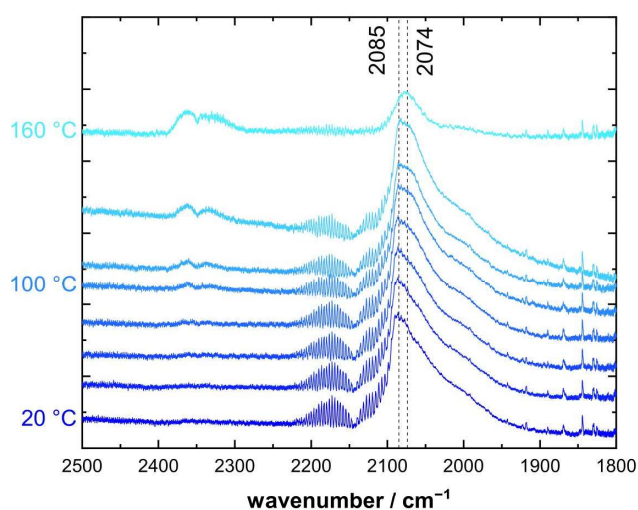


Figure 5. DRIFT spectra of reduced IrO₂@TiO₂ after being heated under an oxidizing (2% O₂/2% CO/96% Ar) reaction feed composition to 160 °C. The spectra show the cool down to 20 °C directly after 160 °C is reached. The temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹. As the catalyst is cooled down, the broad shoulder, indicative of partial reduction, reappears.

As soon as this occurred, the sample is cooled down again, while keeping the oxidizing feed composition. One can recognize in Figure 5 that with decreasing temperature the broad shoulder re-emerges, demonstrating that the catalyst is in fact not fully oxidized at this point.

Figure 6 summarizes the operando DRIFTS experiments of IrO₂@TiO₂ and reduced IrO₂@TiO₂ during the CO oxidation reaction under reducing conditions (1% O₂/4% CO/95% Ar) at various temperatures and includes on-line CO conversion data. The MS data are normalized to their respective maxima, corresponding to a full conversion of O₂ that is equivalent to a 50% conversion of CO.

In DRIFTS of IrO₂@TiO₂ (Figure 6A) a single band is observed as already shown in Figure 3. Here the band position is 2067 cm⁻¹. At 180 °C the broad shoulder starts to appear indicating the beginning of the reduction of the catalyst. This shoulder then keeps growing with the increasing reaction temperature until it reaches down to 1800 cm⁻¹. The CO conversion for IrO₂@TiO₂ (Figure 6B) under reducing conditions starts at 80–100 °C, i.e., slightly earlier than under oxidizing conditions. The conversion then increases in an Arrhenius-like fashion up to about 160 °C. At 180 °C, concurrent with the appearance of the shoulder in DRIFTS, the conversion increases rapidly until it levels off at 220 °C.

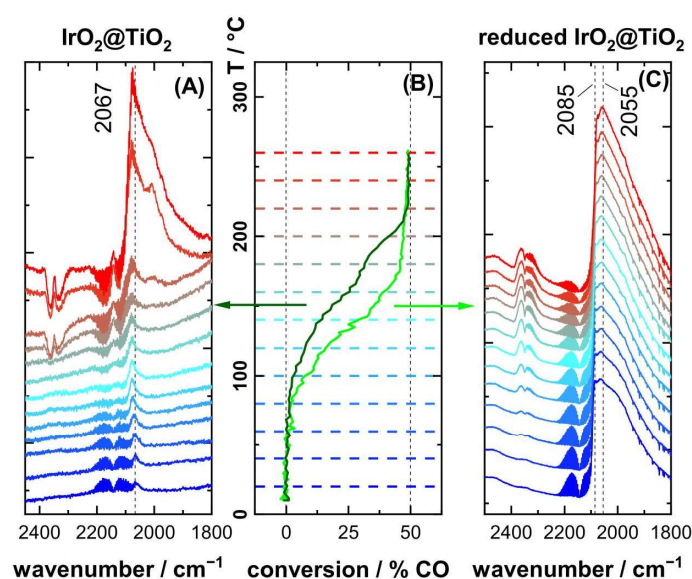


Figure 6. Operando DRIFT spectra of (A) $\text{IrO}_2@\text{TiO}_2$ and (C) reduced $\text{IrO}_2@\text{TiO}_2$ as well as (B) corresponding CO conversion data as measured by MS under reducing (1% O_2 /4% CO/95% Ar) feed composition. For the MS data, the dark green line corresponds to $\text{IrO}_2@\text{TiO}_2$, and the light green line to reduced $\text{IrO}_2@\text{TiO}_2$. The temperature axis of MS and the color code of the dashed lines signify the temperatures of the DRIFT spectra. The temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min^{−1}.

In DRIFTS of the reduced $\text{IrO}_2@\text{TiO}_2$ (Figure 6C) a broad shoulder reaching from 2085 cm^{-1} down to 1800 cm^{-1} is recognizable. The shape differs slightly from the previously shown spectra in Figures 3B and 4C, with a band at 2055 cm^{-1} being more dominant. The shape and position of the bands do not vary significantly throughout the entire temperature range. MS and CO_2 gas phase signals in DRIFTS indicate the onset of CO conversion at about 60 °C. The higher conversion of reduced $\text{IrO}_2@\text{TiO}_2$ relative to $\text{IrO}_2@\text{TiO}_2$ under reducing conditions is at first not as clearly observable in MS as under oxidizing conditions. However, above 80 °C, reduced $\text{IrO}_2@\text{TiO}_2$ shows markedly higher activity. At 180 °C the conversion then levels off in a similar fashion as $\text{IrO}_2@\text{TiO}_2$. Above 220 °C the conversion curves of both samples are practically identical.

4. Discussion

4.1. CO as a Probe Molecule for the Surface Oxidation State of IrO_2

In the literature, signals around 2063–2073 cm^{-1} are reported for CO adsorption on single-crystalline $\text{IrO}_2(110)$ films and polycrystalline IrO_2 supported on Al_2O_3 [36,39,40]. For single-crystalline Ir(111) and metallic Ir supported on Al_2O_3 , CO band positions in the spectral range of 2020–2065 cm^{-1} are found [40–42]. The band positions found in this work (Figure 3A) are similar, with CO adsorption resulting in one distinct signal in the region of 2060–2085 cm^{-1} on both Ir metal and oxide IrO_2 . The exact band position varies slightly so that a characterization of the chemical status of the catalyst by this spectral feature alone does not seem to be possible. The presence of only a single band in DRIFTS found here is, however, quite surprising since the surface of the supported IrO_2 -based particles surely comprises many different facets and adsorption sites. The fact that only one symmetrical band is observed in DRIFTS points toward efficient dipole–dipole coupling of the vibrational modes of all sites. This coupling of different CO species was reported for $\text{RuO}_2(110)$: although CO adsorbs in both the bridge and on-top positions on the mildly

reduced RuO₂(110) surface, only a single CO stretch frequency is observed in RAIRS around 2086 cm⁻¹ [43].

When exposing IrO₂@TiO₂ and Ir⁰ + TiO₂ to a reducing reaction mixture (1% O₂/4% CO/95% Ar) both samples show very similar CO adsorption patterns as reconciled by a broad CO band reaching from 2080 down to 1800 cm⁻¹ in DRIFTS (cf. Figure 3B). The XP spectra in Figure 2 show that under these conditions IrO₂@TiO₂ is partially reduced due to excess CO in the gas feed, while Ir⁰ + TiO₂ is partially oxidized due to the presence of O₂. The oxidation of Ir⁰ + TiO₂ is corroborated by Raman spectroscopy in Figure S6. The full oxidation of Ir⁰ + TiO₂ is, however, inhibited, due to excess CO in the gas feed. The CO adsorption pattern observed for both catalysts is dominated by a spectral feature at 2060–2085 cm⁻¹ with a broad shoulder stretching down to 1800 cm⁻¹. We therefore conclude that this spectral feature is characteristic for partially reduced IrO₂ or partially oxidized Ir, while a single symmetric band is characteristic for pure Ir oxide or pure Ir metal.

4.2. Case Study: Catalytic CO Oxidation

When the IrO₂@TiO₂ and reduced IrO₂@TiO₂ samples were exposed to CO oxidation reaction conditions significant differences in activity were observed. Under both reducing and oxidizing gas feed compositions, reduced IrO₂@TiO₂ reveals a lower onset temperature for CO conversion than IrO₂@TiO₂ by about 50 °C and a higher activity throughout the entire temperature range. Under oxidizing conditions, full conversion is reached for reduced IrO₂@TiO₂ at 160 °C, i.e., 60 °C lower than for IrO₂@TiO₂. Under reducing conditions, the CO conversion saturates at 180 °C and 220 °C for reduced IrO₂@TiO₂ and IrO₂@TiO₂, respectively.

This increase in activity can further be correlated to the partially reduced state of IrO₂@TiO₂ via the characteristic broad shoulder observed in DRIFTS. Under reducing reaction conditions the activity of IrO₂@TiO₂ increases steeply at 180 °C, which is accompanied in DRIFTS by the appearance of the broad CO band at 2050 cm⁻¹ reaching down to 1800 cm⁻¹. Under oxidizing reaction conditions the broad CO shoulder in DRIFTS of reduced IrO₂@TiO₂ disappears as the conversion jumps up at 140 °C, leaving the oxide signal at 2081 cm⁻¹. At first glance, this may suggest a sudden oxidation of the catalyst or a simple desorption of CO due to the high temperature. We conclude, however, that, considering the otherwise higher activity of the reduced catalyst, the disappearance of the broad CO band is due to the reaction of this reactive CO species on the reduced IrO₂@TiO₂ and thus only CO at oxidized parts of the catalyst remain visible in DRIFTS. This interpretation can further be corroborated by cooling the catalyst immediately after the broad shoulder reacted off, as summarized in Figure 5. Here the shoulder reappears as soon as the catalyst is cooled, demonstrating that the reactive CO is re-populated. The disappearance of the reactive CO species is not due to desorption above 140 °C, since this species is shown to be stable up to 260 °C under a reducing feed mixture (cf. Figure 6A,C).

On RuO₂ the mechanism of heterogeneous CO oxidation catalysis has been shown to proceed with the following mechanism [43,44]: (1) CO adsorbing on the catalyst surface; (2) CO combining with O from the oxide lattice to form CO₂; (3) CO₂ desorbing; and (4) O vacancy in the oxide lattice being replenished with O₂ from the gas phase. Both oxides occur in rutile structure and Ru and Ir are close to each other on the periodic table. Therefore, on IrO₂ a similar mechanism is expected to take place. The higher activity of reduced IrO₂ could then be explained in two ways. Firstly, the lattice oxygen in reduced IrO₂ is more facile to be extracted due to lower binding energies. Secondly, oxygen may be more mobile in the defect-rich lattice, allowing active sites to be replenished with oxygen more easily. The latter interpretation would fit well with the recent findings of Martin et al. [4], who reported that subsurface oxygen replacing oxygen on bridge positions plays a role in methane oxidation on IrO₂.

5. Conclusions

Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) is combined with on-line mass spectrometry (MS) to study, with CO serving as probe molecule, the actual oxidation state of a supported $\text{IrO}_2/\text{TiO}_2$ catalyst during the CO oxidation reaction. In doing so, we prepare first pure metal and oxide Ir catalysts to identify characteristic fingerprints in CO stretching vibrations for the pure metallic and the oxidic state of the catalysts, which aid the subsequent interpretation of the CO spectra acquired during the CO oxidation reaction. The CO DRIFT spectra of the pure oxide $\text{IrO}_2/\text{TiO}_2$ samples as well as the pure metal $\text{Ir}^0 + \text{TiO}_2$ are governed by a single mode at 2060 cm^{-1} and 2087 cm^{-1} , respectively. This finding is quite surprising, since CO vibrations from several facets and adsorption sites of the active particles (with varying frequencies) contribute to the DRIFT spectra. It seems that all these vibrational modes couple via dipole interaction, thus culminating in a single band. Quite in contrast, the CO DRIFT spectra of the reduced $\text{IrO}_2/\text{TiO}_2$ and oxidized $\text{Ir}^0 + \text{TiO}_2$ samples show a pronounced broad band ranging from 2085 cm^{-1} to 1800 cm^{-1} , revealing a partially reduced IrO_2 catalyst.

For reduced $\text{IrO}_2/\text{TiO}_2$, the reaction onset and maximum conversion occur at lower temperatures than for $\text{IrO}_2/\text{TiO}_2$. Under oxidizing conditions, CO conversion on $\text{IrO}_2/\text{TiO}_2$ starts at $100\text{--}120\text{ }^\circ\text{C}$ while for reduced $\text{IrO}_2/\text{TiO}_2$ it already starts at $50\text{ }^\circ\text{C}$. Full conversion is accomplished at $220\text{ }^\circ\text{C}$ ($\text{IrO}_2/\text{TiO}_2$) and $160\text{ }^\circ\text{C}$ (reduced $\text{IrO}_2/\text{TiO}_2$). The DRIFT spectra for reduced $\text{IrO}_2/\text{TiO}_2$ under oxidizing conditions evidence that the broad shoulder is consumed preferentially as the catalyst experiences a steep activity increase at $140\text{ }^\circ\text{C}$, thus indicating that this species is the reactive CO on the surface.

Under reducing conditions, the onset of conversion is observed at $80\text{--}100\text{ }^\circ\text{C}$ for $\text{IrO}_2/\text{TiO}_2$ and at $60\text{ }^\circ\text{C}$ for reduced $\text{IrO}_2/\text{TiO}_2$. Maximum conversion is reached at $220\text{ }^\circ\text{C}$ for $\text{IrO}_2/\text{TiO}_2$ and $180\text{ }^\circ\text{C}$ for reduced $\text{IrO}_2/\text{TiO}_2$. $\text{IrO}_2/\text{TiO}_2$ under reducing conditions reveals a steep increase of activity at $180\text{ }^\circ\text{C}$ that is accompanied by a reduction of the catalyst as evidenced by DRIFTS.

The combination of operando DRIFTS and on-line MS therefore provide compelling evidence that the activity of partially reduced $\text{IrO}_2/\text{TiO}_2$ catalysts is significantly higher than that of $\text{IrO}_2/\text{TiO}_2$ under both oxidizing and reducing CO oxidation reaction conditions.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/inorganics11030102/s1>, Figure S1: Light path and temperature Detection; Figure S2: Time response of the MS system; Figure S3: DRIFTS data processing; Figure S4: TEM of $\text{IrO}_2/\text{TiO}_2$; Figure S5: XP spectra of incomplete reduction of $\text{IrO}_2/\text{TiO}_2$ with H_2 ; Figure S6: Raman spectra of Ir^0 before and after reducing CO oxidation conditions; Table S1: XPS fit parameters; Figure S7: Blank DRIFT spectra of rutile- TiO_2 without active component; Figure S8: DRIFT spectrum of CO adsorption on $\text{Ir}^0 + \text{TiO}_2$ after oxidative pretreatment.

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4.3 Publication III: Active Phase of IrO₂ in the Catalytic CH₄ Combustion Reaction: Operando Infrared Spectroscopy and On-Line Mass Spectrometry

This study utilizes the insights gained in **Publication II** to elucidate the most active phase for CH₄ oxidation over IrO₂. The presence of CO on the surface allows for insight into the oxidation state of the catalyst under oxidizing and reducing reaction conditions for fully oxidized and partially reduced IrO₂ catalysts. The presence of CO under reaction conditions further proves that CO is in fact an intermediate of the CH₄ oxidation. Whenever CO is observed the band pattern observed in DRIFTS indicates a partially reduced surface, while no CO is observed when the catalyst is in a fully oxidized state. In conjunction with previous studies this finding demonstrates that CO is no intermediate on fully oxidized single-crystalline IrO₂(110), thus pointing towards a change in reaction pathway in dependence of the oxidation state of the catalyst. The conversion curves reveal partially reduced IrO₂ being significantly more active than its fully oxidized counterpart. However, under reducing conditions the IrO₂ surface is depleted of oxygen, thus hampering the activity at high temperatures. The highest activity is achieved by partially reduced IrO₂ under oxidizing condition. However, under these conditions the partially reduced IrO₂ will slowly oxidize, losing its superior activity as a consequence. It is, therefore, demonstrated that activity and reaction mechanism can be manipulated by altering the oxidation state of IrO₂.

H. Over and I devised the experimental schedule. L. Glatthaar performed the XPS measurements. I prepared the samples and performed the DRIFTS experiments. H. Over, and I contributed through scientific discussions of the data. H. Over and I wrote the draft version of the manuscript. All authors revised the manuscript and have given approval to the final version.

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Active Phase of IrO₂ in the Catalytic CH₄ Combustion Reaction: Operando Infrared Spectroscopy and On-Line Gas Analysis

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Abstract:

With operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and on-line gas analysis we studied the catalytic methane combustion over 2 mol% IrO₂ supported on rutile TiO₂ under reducing (CH₄:O₂ =1:1) and oxidizing reaction conditions (CH₄:O₂ =1:4). Two types of catalysts are considered: the samples are pretreated at 320°C either with O₂ (ox-IrO₂@TiO₂) to ensure full oxidation or with CH₄ (red-IrO₂@TiO₂) to partially reduce IrO₂. Ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ are stable under oxidizing and reducing methane oxidation conditions, respectively. DRIFTS indicates that under reducing conditions CO is formed on red-IrO₂@TiO₂, while no CO formation is observed for ox-IrO₂@TiO₂ under oxidizing conditions. Methane oxidation under reducing conditions transforms ox-IrO₂@TiO₂ into red-IrO₂@TiO₂ showing strong CO bands and a higher activity than oxidized IrO₂. This observation is in stark contrast to methane oxidation studies over single crystalline IrO₂(110), thus manifesting a materials gap. Highest methane conversion is achieved with red-IrO₂@TiO₂ under oxidizing reaction feed. The formation of adsorbed CO on the catalyst evidences that the reaction mechanism proceeds via the formaldehyde intermediate.

Keywords: IrO₂; methane combustion; active phase; operando Infrared spectroscopy; on-line gas analysis;

1. Introduction

In general, new catalysts are found by screening potential powder sample materials. In a next step, surface science experiments and theory may be conducted for single crystalline model system to unveil mechanistic details. In this way supported Pd- and Pt-based catalysts were identified to be efficient catalyst for the methane oxidation,^{1–8} and subsequently various surface science groups have studied mechanistic details of the methane oxidation.^{9–15}

The exceptional activity of IrO₂ in methane activation is one of the rare cases where the catalyst has been identified first by surface science studies of single crystalline IrO₂(110). IrO₂ is a surprisingly good methane oxidation catalyst that is able to activate methane at temperatures as low as 150 K. This was first predicted based on DFT calculations¹⁶ and later corroborated by surface science experiments of IrO₂(110) films grown on Ir(100).¹⁷ The first activity experiments in a flow reactor were reported by Khalid et al.¹⁸ Methane oxidation over IrO₂ powder samples indicates that the low-temperature activity of IrO₂ cannot be utilized for the partial oxidation of methane to produce value-added chemicals, but rather leads to complete oxidation of methane to form CO₂ and water.

In situ X-ray diffraction (XRD), Raman spectroscopy, and diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments in combination with density functional theory (DFT) calculations were conducted to study methane activation over IrO₂ nanoparticles upon pure methane exposure.¹⁹ It turned out that methane reduces IrO₂ to metallic Ir with a much lower activity for methane activation. The highest activity towards methane activation was found to be partially reduced IrO₂. Martin et al.²⁰ studied the reduction of single crystalline IrO₂(110) by pure methane exposure at higher temperatures of 500–600 K with in-situ X-ray photoelectron spectroscopy (XPS) and reported partial reduction of IrO₂(110). The formed metallic Ir was shown to decrease the methane activity. We note that the partial reduction of IrO₂(110) can also be induced by temperature treatment of 400–500 K under UHV conditions.^{21,22}

Recently, Martin et al. studied the methane activation of single crystalline IrO₂(110) employing operando ambient pressure XPS.²³ It turned out that even little oxygen in the reaction feed (CH₄ : O₂=10:1) suffices to maintain IrO₂(110) grown on Ir(100) fully oxidized. This was considered as strong evidence that the catalytically active phase under typical methane oxidation conditions is IrO₂.

In the present study the catalytic methane oxidation on IrO₂ supported on rutile TiO₂, employing operando DRIFTS and on-line gas analysis. Operando DRIFTS is able to monitor the oxidation state of IrO₂ via specific CO vibration frequency as recently demonstrated for the CO oxidation over the same catalyst,²⁴ and DRIFTS is able to identify reaction intermediates. Our study demonstrates that the most active phase in the methane oxidation is the partially reduced IrO₂, rather than the oxidized IrO₂ phase as found for single crystalline IrO₂(110). This conflicting results manifests an apparent materials gap in that conclusion drawn from single crystalline surface may be not transferrable to supported powder samples.

2. Experimental Details

Preparation and characterization of the samples employed in this work was published in previous work.^{24,25} To briefly summarize, supported IrO₂ on TiO₂ with a loading of 2 mol% was prepared *via* the Pechini synthesis. DRIFTS needs a reflective matrix (TiO₂) when the material under investigation (IrO₂) absorbs IR radiation. The samples are pretreated under 4% O₂ to ensure full oxidation or 4% CH₄ to partially reduce IrO₂ at 320 °C for 1 h in situ in the DRIFTS reactor before measurements are performed. These samples are referred to ox-IrO₂@TiO₂ and red-IrO₂@TiO₂, respectively, throughout the manuscript.

The reactor used for the present study was designed and built in house and described in detail in previous publications.^{24,26} It consists of a gas supply controlled by mass flow controllers connected to a custom designed reactor cell made from 1.4742 Ni-free steel and that is integrated into a Bruker v70 spectrometer to conduct operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). The effluent is analyzed by a gas analyzer (*GS IRA8000*). The total flow employed in all experiments is 100 sccm with a heating ramp of 1.8 K·min⁻¹. **Table 1** compiles the feed compositions for the various experiments.

Table 1: Gas compositions for different methane oxidation experiments.

Reaction conditions	Ar / %	O ₂ / %	CH ₄ / %
Oxidizing	95	4	1
Reducing	98	1	1
CH ₄ only	96	-	4

The X-ray photoelectron spectroscopy (XPS) characterization is performed on a PHI VersaProbe IV instrument, employing a photon energy of 1486.6 eV (Al K α line).

3. Experimental Results

In this study CO serves as a probe molecule to monitor the surface oxidation state of IrO₂. This is possible during the oxidation of CH₄ as CO is identified to be a reaction intermediate on red-IrO₂@TiO₂. The interpretation of DRIFTS band position and shape in terms of the oxidation state of the catalyst has been recently demonstrated by Timmer *et al.*²⁴. A signal starting around 2085 cm⁻¹ or lower with a broad shoulder reaching down to 1800 cm⁻¹ is indicative of a partially reduced IrO₂ surface (red-IrO₂@TiO₂).

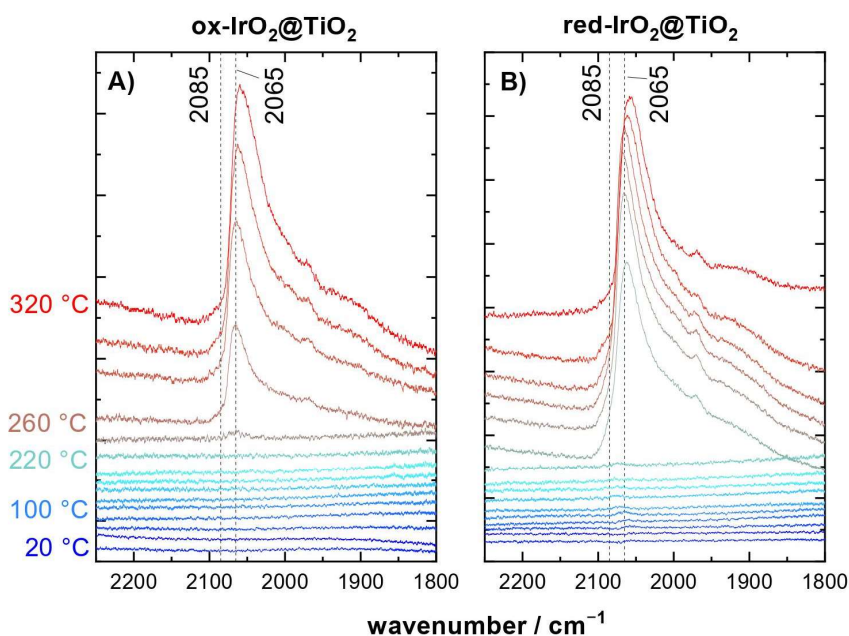


Figure 1: Operando DRIFTS spectra of A) ox-IrO₂@TiO₂ as well as B) red-IrO₂@TiO₂ under 4% CH₄ in Ar. The bands shown correspond to CO adsorbed on the catalyst surface. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

Figure 1 depicts the DRIFT spectra in the region of adsorbed CO on ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ under 4% CH₄ in Ar while being heated stepwise to 320 °C. In terms of CO functioning as an indicator for the oxidation state of the catalyst it would be expected to see a symmetric band in the region of 2085 to 2065 cm⁻¹ for fully oxidized IrO₂ while a partially reduced IrO₂ surface would show a broad shoulder reaching down to about 1800 cm⁻¹.²⁴ For low temperatures, no spectral features of CO can be seen in **Figure 1**. Only above a threshold temperature, both samples exhibit a broad asymmetric band as soon as CO is formed as reaction intermediate in the methane activation process, while no spectral feature of gaseous CO is observed in DRIFTS. The 2085 cm⁻¹ band, indicative of CO adsorbed on oxidized IrO₂ surfaces, can merely be discerned as a small shoulder band. The broad asymmetric shoulder (2065-1800 cm⁻¹) indicates clearly that both IrO₂ samples are in the partially reduced state upon methane activation at higher temperatures. The most striking difference between the DRIFT spectra of ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ is that the CO band emerges at about 40 °C lower temperatures on red-IrO₂@TiO₂ (200°C instead of 240°C). For both samples no further surface species, other than possibly some minor carbonate and OH species, can be identified in DRIFTS under 4% CH₄ as is summarized in **Figure S1**.

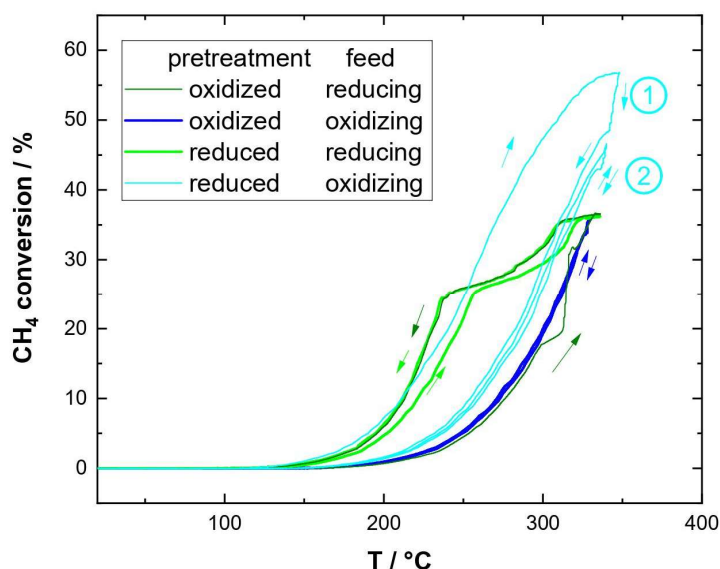


Figure 2: Conversion plots as recorded by the gas analyzer for ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ under oxidizing (1% CH₄ / 4% O₂ / 95% Ar) and reducing (1% CH₄ / 1% O₂ / 98% Ar) reaction feed. Heating and cooling curves are shown with the arrow denoting the direction. For red-IrO₂@TiO₂ under oxidizing conditions two reaction cycles are shown (cyan (1) and (2)). For the other conditions, the second cycle is omitted for clarity reasons, since the second cycle follows the cooling curve of the first cycle.

Both ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ were heated to 340 °C and then cooled back to room temperature under reducing or oxidizing feed compositions. The samples are held at the maximum temperature (340 °C) for 30 min to give the catalyst time to reach equilibrium. The corresponding conversion plots are summarized in **Figure 2**. For ox-IrO₂@TiO₂ under oxidizing conditions methane conversion starts at around 200 °C and then increases smoothly till reaching a maximum of 37 % at 340 °C. During cool down it follows exactly the same trajectory with no obvious hysteresis.

For red-IrO₂@TiO₂ under reducing condition methane conversion starts at 150 °C and increases steadily up to 260 °C, where the increase of conversion with rising temperature slows down considerably. Above 300 °C methane conversion accelerates before reaching its maximum conversion of 37 %. During cooling a slight hysteresis occurs although the conversion follows the same general trend as during the heating ramp. The observed hysteresis is likely due to reaction heat that cannot properly be removed from the catalyst bed.

When ox-IrO₂@TiO₂ is heated under reducing reaction conditions the conversion curve follows the one for oxidizing conditions almost exactly with the only difference being a small light-off around 300 °C. The conversion reaches again a maximum at 37 %. During cool down the curve follows closely the one from red-IrO₂@TiO₂ under reducing conditions. Obviously, the ox-IrO₂@TiO₂ sample has transformed into red-IrO₂@TiO₂ during methane oxidation under reducing conditions when increasing the reaction temperature.

Highest conversion is accomplished with red-IrO₂@TiO₂ under oxidizing conditions. Here at first the conversion follows that of red-IrO₂@TiO₂ under reducing conditions. However, no slowing of the conversion increase is observed, instead the conversion increases smoothly up to about 300 °C, where it starts to slow down and finally reaches a maximum conversion of 57 %. When the red-IrO₂@TiO₂ catalyst is held at 340 °C under oxidizing conditions, the conversion declines to 48 %. During subsequent cool down the conversion is significantly lower than during heating. A second reaction cycle under the same conditions is shown in **Figure 2**. The conversion is slightly lower than during cooling in the first cycle and approaches the one of ox-IrO₂@TiO₂ under oxidizing conditions. The maximum conversion is with 46 % still substantially higher than that of ox-IrO₂@TiO₂ under oxidizing conditions. When red-IrO₂@TiO₂ is held at 340 °C under oxidizing conditions for a long time it will return to its oxidized state (cf. **Figure S2**).

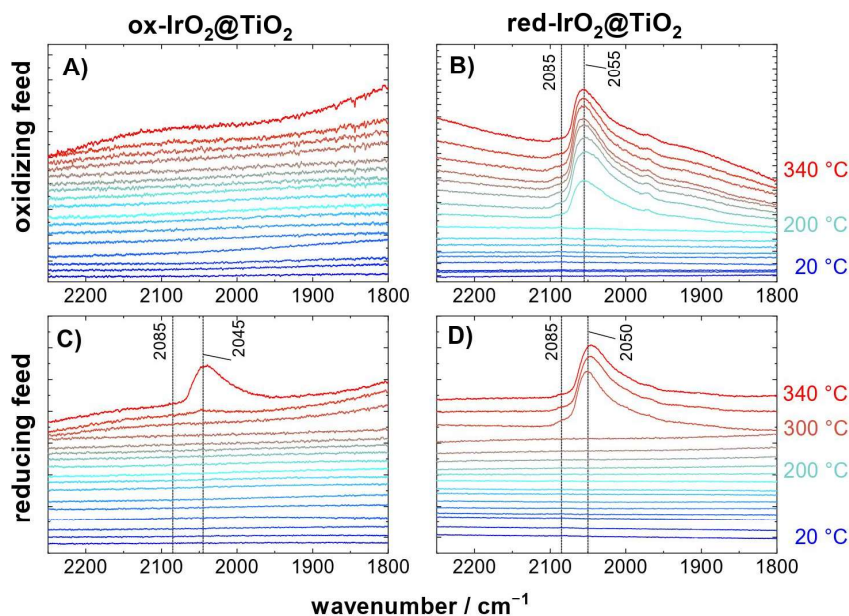


Figure 3: Operando DRIFT spectra of ox-IrO₂@TiO₂ under A) oxidizing and C) reducing feed compositions as well as red-IrO₂@TiO₂ under B) oxidizing and D) reducing feed compositions. The bands shown correspond to CO adsorbed on the catalyst surface. The temperature at which CO formation can be observed varies according to pretreatment and feed composition. Temperature increment between consecutive spectra is 20 °C, while the heating ramp is 1.8 K·min⁻¹.

Figure 3 summarizes the DRIFTS measurements recorded during the first heat up of the reaction cycles shown in **Figure 2**. For ox-IrO₂@TiO₂ under oxidizing reaction conditions adsorbed CO cannot be discerned in DRIFTS. From **Figure 1** we know that CO is formed, however, the supplied O₂ oxidizes the formed reaction intermediate CO instantaneously to CO₂. Under reducing conditions adsorbed CO can be observed only at 340 °C for ox-IrO₂@TiO₂. The CO band is at 2045 cm⁻¹, at slightly lower wavenumber than observed in **Figure 1**, with a slight shoulder reaching down to lower wavenumbers, thus evidencing a partially reduced surface. Here no signal at 2085 cm⁻¹, that is indicative of an oxidized surface, can be discerned. The 2085 cm⁻¹ band emerges, however, during the second reaction cycle as indicated in **Figure S3**.

For red-IrO₂@TiO₂ the band positions of CO for reducing and oxidizing feeds are similar, with the main band occurring at 2050 cm⁻¹ and 2055 cm⁻¹, respectively that is assigned to CO on a partially reduced surface and a small band at 2085 cm⁻¹ for both reaction conditions that is ascribed to CO on ox-IrO₂@TiO₂. The main difference between the two reaction conditions is the on-set temperature at which CO starts to emerge in DRIFTS. For reducing conditions bands start to appear at 300 °C, while for oxidizing conditions adsorbed CO appears already at 200 °C. The low temperature formation of adsorbed CO is paralleled with the higher activity of the red-IrO₂@TiO₂ under oxidizing conditions (cf. **Figure 2**). Extended DRIFTS spectra in **Figure S4** show some small bands around 2940 cm⁻¹ due likely to formates²⁷ and some bands below 1750 cm⁻¹ that likely originate from carbonates.

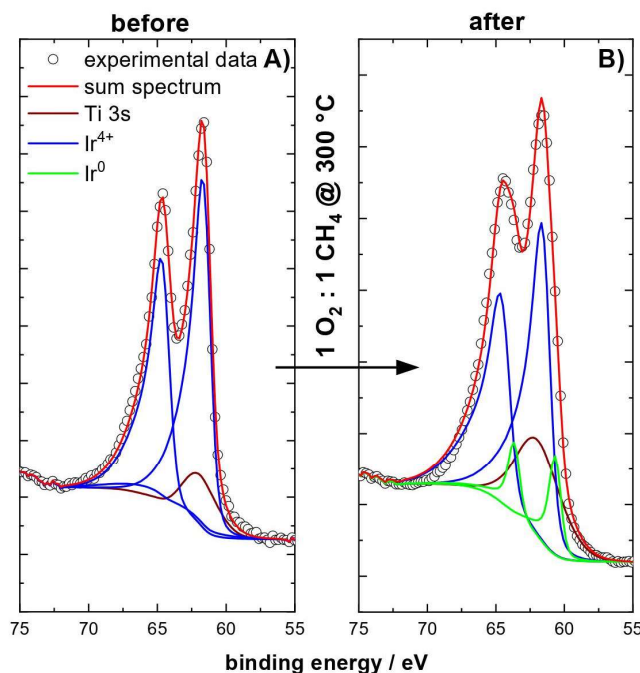


Figure 4: Ir 4f XPS spectra of IrO₂@TiO₂ before and after being exposed to reducing CH₄ oxidation conditions (1% CH₄ / 1% O₂ / 98% Ar) at 300 °C for 1h. To prevent re-oxidation at lower temperatures the samples is cooled down with 15 K·min⁻¹ without changing the feed. The fit parameters for the decomposition of the experimental XPS data (circles) are provided in **Table S1** of the Supplementary Materials.

Figure 4 summarizes XP experiments of ox-IrO₂@TiO₂ in the 4f region before and after exposure to reducing CH₄ oxidation conditions at 300 °C. Before methane oxidation reaction only Ir⁴⁺ signals can be detected. This shows that the sample consists of oxidic IrO₂ only. After methane oxidation reaction, additional spectral features appear in the Ir 4f spectrum that corresponds to metallic iridium Ir⁰.

Obviously part of IrO_2 is reduced that is in full agreement with conclusions drawn from the DRIFTS experiment in **Figure 3**.

4. Discussion

The presence of CO on the surface when the reaction feed only contains CH_4 is clear evidence of methane activation, while simultaneously providing information on the chemical state of the surface of the catalyst. The broad CO bands reaching down to 1800 cm^{-1} in **Figure 1** demonstrate that the IrO_2 catalyst is in a partially reduced state. Since only CH_4 is exposed, the oxygen of adsorbed CO needs to come from the lattice IrO_2 , thus chemically reducing the oxide. In contrast, adsorbed CO on pure oxide is not observed in DRIFTS that would lead to a symmetric peak in the region of 2085 to 2065 cm^{-1} . Therefore, we conclude that adsorbed CO is mainly produced from CH_4 activation when the catalyst surface is in a partially reduced state above $260\text{ }^\circ\text{C}$. A temperature of $260\text{ }^\circ\text{C}$ is in good agreement with the findings of Martin *et al.*²⁰ who reported a reduction onset temperature for single crystalline $\text{IrO}_2(110)$ of $230\text{ }^\circ\text{C}$. CO adsorption bands appear on red- $\text{IrO}_2@\text{TiO}_2$ at $40\text{ }^\circ\text{C}$ lower temperatures than on its oxidized counterpart, thus evidencing that the reduction process of IrO_2 occurs at $260\text{ }^\circ\text{C}$.

The conversion plots in **Figure 2** indicate that the activity of red- $\text{IrO}_2@\text{TiO}_2$ is higher than that of ox- $\text{IrO}_2@\text{TiO}_2$ with an onset temperature for methane conversion of red- $\text{IrO}_2@\text{TiO}_2$ being about $40\text{ }^\circ\text{C}$ lower than for ox- $\text{IrO}_2@\text{TiO}_2$. Under reducing conditions ($\text{O}_2 : \text{CH}_4 = 1 : 1$), ox- $\text{IrO}_2@\text{TiO}_2$ reveals significantly enhanced conversion during cool down that parallels methane conversion on red- $\text{IrO}_2@\text{TiO}_2$. These findings conflict clearly with studies of Martin *et al.*²³, who reported that the stoichiometric $\text{IrO}_2(110)$ surface is stable up to 650 K for reaction mixture of $\text{O}_2:\text{CH}_4$ ratios as low as 1:9. We think that this contradiction expresses an apparent materials gap between the single crystalline $\text{IrO}_2(110)$ film and multi-faceted IrO_2 nanoparticles in the present study. We note that some evidence for increased activity of the partially reduced $\text{IrO}_2(110)$ was also provided by Martin *et al.*²³ in the supporting information: for a $\text{O}_2:\text{CH}_4$ ratio of 1:19 at 650 K reduction of $\text{IrO}_2(110)$ had not been observed for the first 15 minutes, while thereafter the reduction of IrO_2 took place rapidly concomitantly with a sharp rise in activity.

Under oxidizing reaction condition the conversion plot of ox- $\text{IrO}_2@\text{TiO}_2$ is stable throughout the temperature cycle, i.e., the conversion curves are practically identical while being heated and cooled as well as during subsequent cycles. A similar stability is encountered with red- $\text{IrO}_2@\text{TiO}_2$ under reducing reaction conditions. At lower temperatures the conversion of red- $\text{IrO}_2@\text{TiO}_2$ under reducing conditions is higher than that of ox- $\text{IrO}_2@\text{TiO}_2$ under oxidizing reaction conditions, but approaches in both cases a final conversion of 37% at $340\text{ }^\circ\text{C}$. When red- $\text{IrO}_2@\text{TiO}_2$ is exposed to oxidizing reaction mixture the catalyst reveals similar conversion at low temperatures as under reducing reaction conditions, while at higher temperatures the conversion is substantially higher, reaching the highest conversion of all samples with 57 % at $340\text{ }^\circ\text{C}$. Obviously, the partially reduced surface suffers from O depletion at the catalyst surface under reducing conditions and therefore is not able to maintain high conversion, while the oxidizing reaction feed supplies the red- $\text{IrO}_2@\text{TiO}_2$ steadily with oxygen to sustain high methane conversion. However, under oxidation conditions the red- $\text{IrO}_2@\text{TiO}_2$ sample slowly oxidizes and deactivates as observed during cool down and subsequent reaction cycles, approaching ultimately the conversion curve of ox- $\text{IrO}_2@\text{TiO}_2$ under oxidizing feed.

Previous studies of Kim *et al.*²⁸ and Martin *et al.*²⁰ reported that oxygen atoms adsorbing on-top (O_{ot}) of coordinatively unsaturated Ir sites (Ir_{cus}) are especially active in CH_4 activation. The increased activity of red- $\text{IrO}_2@\text{TiO}_2$ under oxidizing conditions can, therefore, be traced to an accumulation of the more reactive O_{ot} species. As the transformation of O_{ot} to oxygen in bridge positions (O_{br}) is facile on the IrO_2 surface²⁹ any O_{ot} species forming on the reduced IrO_2 surface may quickly transform to the less active O_{br} species, associated with a lower activity. Under oxidizing conditions, however, enough oxygen is

supplied from the gas phase to maintain a high enough coverage of O_{ox} species and therefore results in an increased activity.

The higher activity of red-IrO₂@TiO₂ in methane oxidation is also reflected in the DRIFT spectra that are taken during the conversion plots (cf. **Figure 3**). Since adsorbed CO is readily oxidized in the presence of oxygen, the appearance of CO bands is shifted to higher temperatures than under pure CH₄ exposure as indicated in **Figure 1**. For red-IrO₂@TiO₂ under reducing conditions, adsorbed CO in DRIFTS is observed at 300 °C that is 40 °C lower in temperature than for its oxidized counterpart. In accordance with the observed higher conversion, red-IrO₂@TiO₂ under oxidizing conditions shows CO bands above 200 °C. For the red-IrO₂@TiO₂ under both reducing and oxidizing conditions, the main peaks in DRIFTS at 2050 and 2055 cm⁻¹ are significantly lower than 2065 cm⁻¹, with a shoulder band at 2085 cm⁻¹. While the main CO band position at 2065 cm⁻¹ can be assigned to partially reduced surface, the small shoulder peak at 2085 cm⁻¹ suggests that still oxidized regions are present on the catalyst surface. When CO is added to the reaction feed during cool down of the catalysts under reducing methane oxidation conditions (1% CH₄ / 1% O₂ / 1% CO / 97 % Ar; cf. **Figure S5**), the band at 2085 cm⁻¹ dominates at low temperatures (< 140 °C) where CH₄ oxidation is suppressed, supporting the assignment of CO being adsorbed on oxidic IrO₂ as reported Ref.24. In the temperature region from 280 °C to 200 °C no CO band can be detected in **Figure S5** since adsorbed CO is efficiently removed from the surface by oxidation to CO₂.

For ox-IrO₂@TiO₂ under oxidizing conditions CO bands are not discernible since CO reacts off quicker than it is produced from CH₄ activation. For ox-IrO₂@TiO₂ under reducing conditions adsorbed CO occurs in DRIFTS above 340 °C. Note that here no 2085 cm⁻¹ band, corresponding to an oxidized surface, can be observed while the main band position of 2045 cm⁻¹ is in the spectral region of the partially reduced surface state. The 2085 cm⁻¹ signal is in fact discernible in a second reaction cycle as depicted in **Figure S3**. The absence of the 2085 cm⁻¹ band in the first cycle is explained by the oxide surface that is covered by oxygen and therefore, not able to provide adsorption sites for CO. In the second cycle some oxygen from the fully oxidized IrO₂ surface has been reacted off, thus offering adsorption sites for CO.

The higher activity of red-IrO₂@TiO₂ can be understood in terms of a cooperative interaction of coordinatively unsaturated (cus) metal ions and adjacent oxygen playing a dominant role in the C-H bond cleavage on transition metal oxides.^{11,16,17,20,30–32} A partially reduced IrO₂ provides a large number of cus-sites while providing sufficient surface oxygen sites to take up the abstracted hydrogen.

The presence of CO on the surface under reaction conditions has strong implications on the reaction pathway. Especially for red-IrO₂@TiO₂ under oxidizing condition it is surprising that CO remains observable in DRIFTS at high temperatures above 200 °C, as CO oxidation should be rather fast under these conditions.²⁴ Consequently, CO has to be produced at a comparably high rate to be observable. Multiple pathways for the oxidation of methane on the surface are conceivable following different sequences of abstracting hydrogen and adding oxygen to the carbon. One could divide those pathways into two groups. First, one oxygen is added before abstracting the rest of hydrogen thus proceeding through a formaldehyde like (H₂CO) reaction intermediate. Secondly, two oxygen atoms are added before abstracting the last H, thus forming a formic acid like (HCO₂) intermediate. This reaction intermediate would not allow for production of adsorbed CO. Martin *et al.*²³ reported that on single crystalline IrO₂(110) the formation of HCO₂ is dominant and no adsorbed CO is formed. This finding is very different from the case of IrO₂@TiO₂ nanoparticles, where methane activation and oxidation lead to a partially reduced catalyst onto which CO is formed faster than it is consumed by oxidation or desorption. However, this finding does not necessarily conflict with the single crystalline IrO₂(110) study, since IrO₂(110) was shown to be not reduced. The fact that CO is observable on partially reduced

IrO₂ thus points towards the formaldehyde pathway being dominant in the methane oxidation. This conclusion is in agreement with Liu *et al.*¹⁹ who identified the CH₂O species on IrO₂ by Raman spectroscopy during pure methane exposure.

5. Conclusions

The oxidation of methane over IrO₂ supported on TiO₂ (IrO₂@TiO₂) is studied for various feed compositions and temperatures by employing operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and on-line gas analysis. Adsorbed CO on fully oxidized IrO₂@TiO₂ is not observed in DRIFTS that would result in a symmetric band at ca. 2085 cm⁻¹. Adsorbed CO is, however, detected when CO-DRIFTS indicates that IrO₂ is in a partially reduced state as reconciled with the appearance of a band in the region of 2065 cm⁻¹ with a broad shoulder reaching to lower wavenumbers of 1800 cm⁻¹. Partially reduced IrO₂@TiO₂ exhibits a higher activity than fully oxidized IrO₂. Previous studies showed that single crystalline IrO₂(110) remains fully oxidized under CH₄:O₂ as high as 9:1 at 650 K.⁶ This is not the case for the powder samples IrO₂@TiO₂, as demonstrated by DRIFTS and the XPS spectra, thus disclosing an apparent materials gap. When the reaction is run with a reducing feed over partially reduced IrO₂@TiO₂ the conversion levels off at 37 %. The highest conversion of 58 % is reached when partially reduced IrO₂@TiO₂ is exposed to an oxidizing reaction conditions. Obviously, the reducing feed is unable to supply the partially reduced IrO₂ surface with enough oxygen to maintain a high methane conversion. Previous surface science studies⁶ demonstrated that on single crystalline IrO₂(110) the reaction pathway proceeds preferentially through the formate (H₂CO₂) intermediate, excluding the formation of adsorbed CO. The fact that adsorbed CO is observed on partially reduced IrO₂@TiO₂ powder samples evidences that the reaction takes place through formation of the formaldehyde (CH₂O) species. Altogether, the reaction mechanism of methane oxidation depends therefore critically on the oxidation state of the IrO₂ catalyst.

Acknowledgement: PT and HO acknowledge financial support by the DFG (SPP2080 - 493681475).

Supporting information: The Supporting Information is available free of charge. In the supporting information the reader finds fitting parameter of Ir4f XP spectra; survey DRIFT spectra of ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ under 4% methane in Ar; Time evolution of DRIFT spectra of red-IrO₂@TiO₂ under oxidizing reaction conditions; DRIFT spectra of ox-IrO₂@TiO₂ under reducing reaction conditions during second temperature cycle; survey DRIFT spectra of ox-IrO₂@TiO₂ and red-IrO₂@TiO₂ under oxidizing reaction conditions; Operando DRIFT spectra of red-IrO₂@TiO₂ under reducing reactions conditions with the addition of CO.

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5 Appendix

5.1 Supporting Information on Publication I

Table S1. XPS fit parameters.

<i>Species</i>	<i>Peak</i>	<i>Binding energy</i>	<i>FWHM</i>	<i>Fitting parameters</i>
Ru	3d _{5/2}	279.9	0.93	LF(0.8,1.25,500,180)
	3d _{3/2}	284.1	0.93	LF(1.01,1.25,500,50)
RuO ₂	3d _{5/2}	280.6	0.9	LF(0.4,1,45,280)
	3d _{3/2}	285.4	1.2	LF(0.4,1,45,280)
	3d _{5/2} satellite	282.4	2.15	LF(0.6,1,45,280)
	3d _{3/2} satellite	286.6	2.20	LF(0.4,1,45,280)
C	1s	285.1	1.36	GL(30)
C-oxid	1s	288.8	1.00	GL(30)

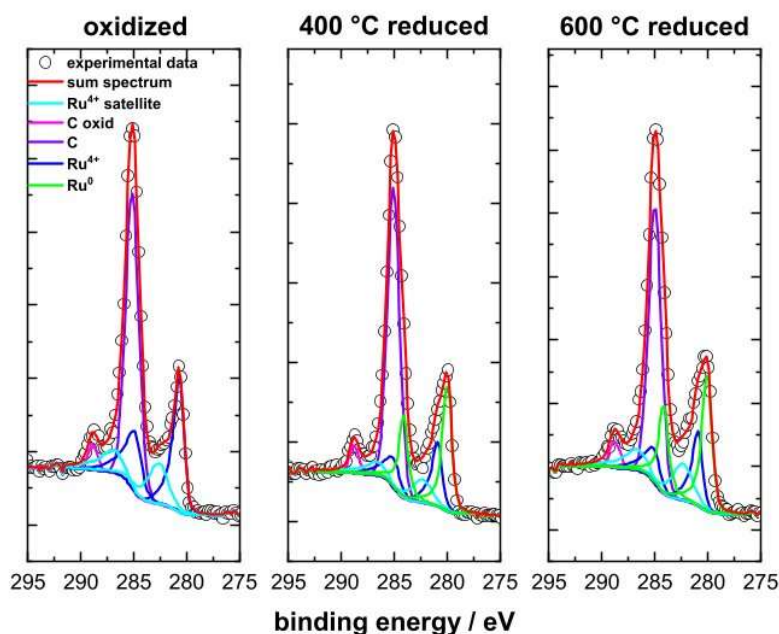


Figure S1. Ru 3d XP spectra of oxidized and reduced RuO₂. The reduction was carried out under 4% H₂ in Ar for 12 h at the stated temperatures.

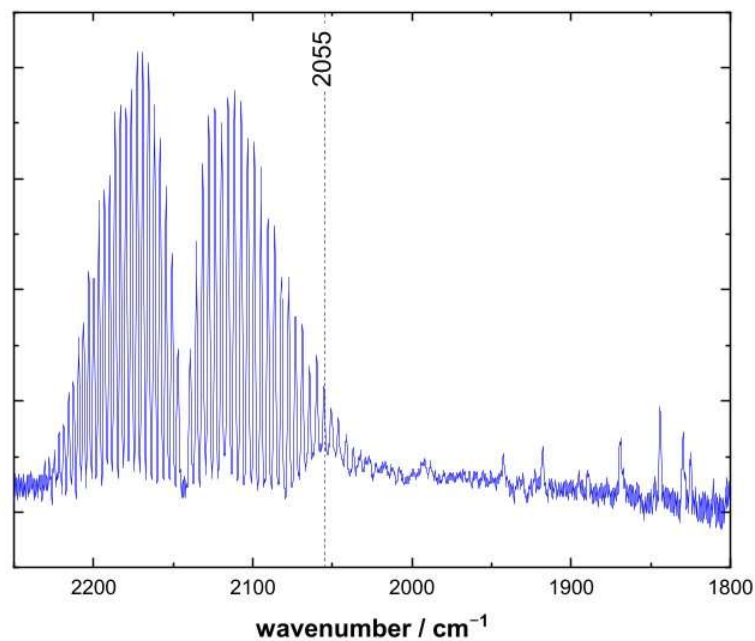


Figure S2. DRIFTS spectrum of CO adsorption on Ru^0+TiO_2 , which has after oxidative pretreatment under 4% O_2 at 300 °C for 12h. As previously shown for $\text{RuO}_2@\text{TiO}_2$ only one band without shoulder is observed.

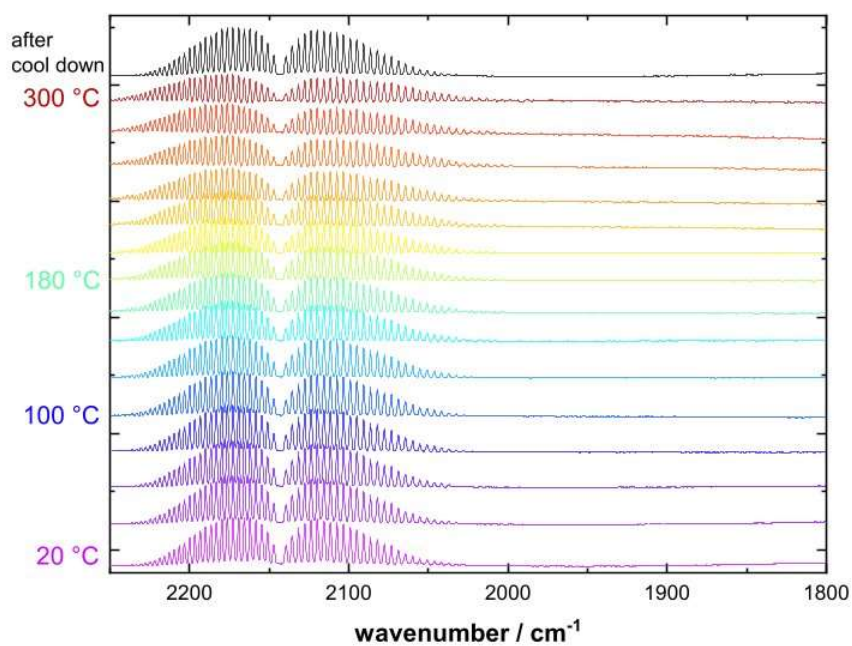


Figure S3. IR spectra of pre-oxidized TiO_2 heated in a CO atmosphere. CO adsorption bands are not observed, while the RoVi finr structure of CO gas appears between 2100-2200 cm^{-1} .

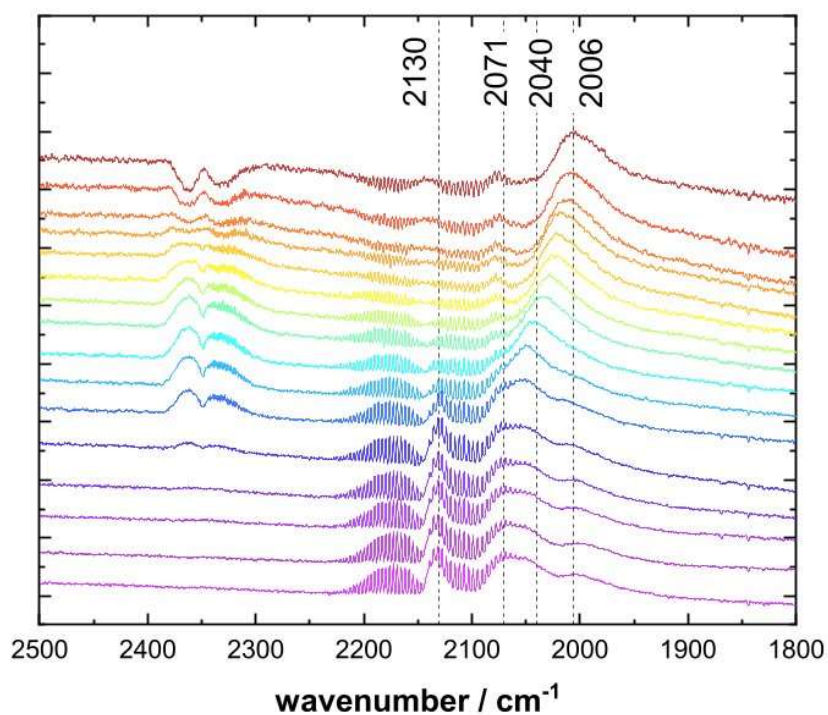


Figure S4. Operando DRIFT spectra of reduced-RuO₂@TiO₂ during cool down under reducing (1% O₂/4% CO/95% Ar) reaction feed composition. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

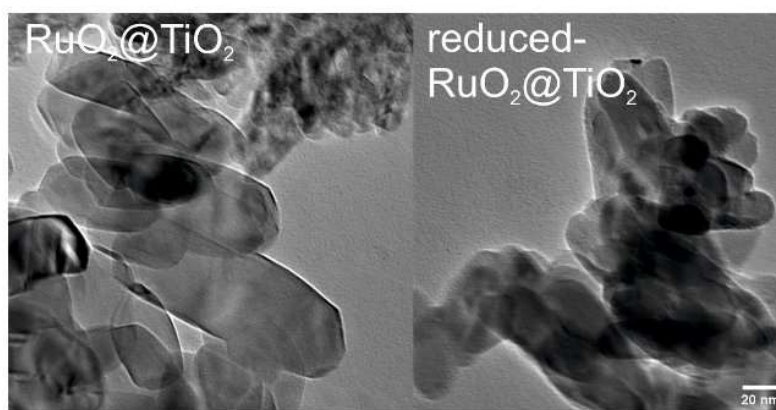


Figure S5. TEM micrographs of RuO₂@TiO₂ (left) before and (right) after reduction. The particles seen correspond to TiO₂ with the RuO₂ not being clearly visible. No morphological changes can be identified after reduction.

5.2 Supporting Information on Publication II

Supporting Information

Article

Operando CO Infrared Spectroscopy and On-Line Mass Spectrometry for Studying the Active Phase of IrO₂ in the Catalytic CO Oxidation Reaction

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Light path and Temperature Detection

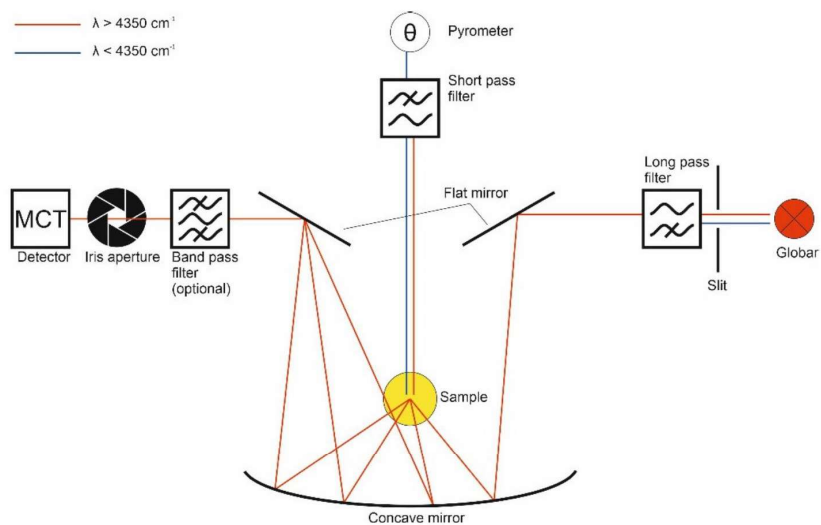


Figure S1. Scheme of the light path through spectrometer and reactor.

Time response of the MS system

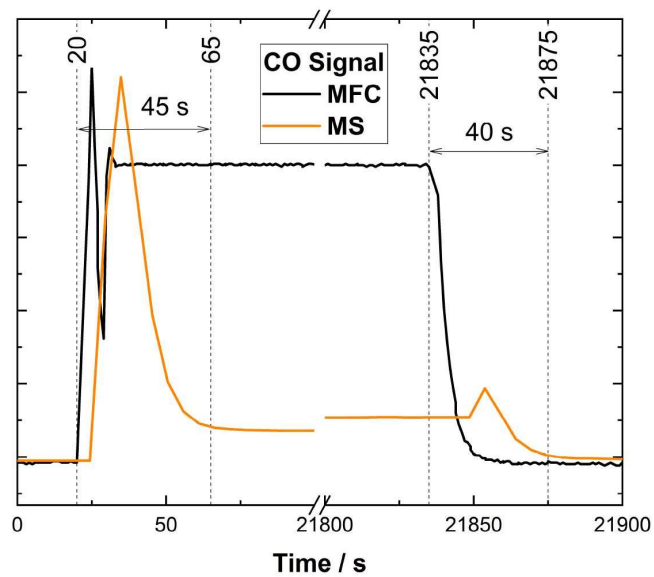


Figure S2. Delay between MFC gas flow and mass spectrometer (MS) signal of CO.

DRIFTS data processing

For all DRIFTS experiments, blank spectra of the catalysts are recorded for every temperature under pure argon conditions during cool down after the pretreatment procedure. Spectra are recorded with 20 scans at 1 cm⁻¹ resolution every 100 s.

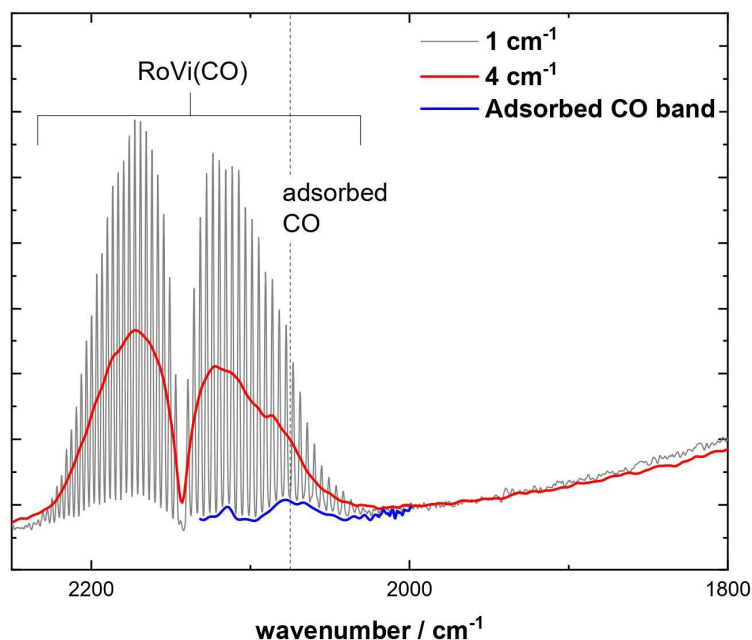


Figure S3. Example of high (1 cm⁻¹) and low (4 cm⁻¹) resolution spectra with adsorbed and gas phase CO bands on IrO₂@TiO₂ at 20 °C under 4% CO. In the 1 cm⁻¹ spectrum (black) the rotational fine structure is resolved allowing for a clear identification of the adsorbed CO band (shown in blue).

The high resolution enables to resolve the rotational fine structure (coupling of rotation with vibration: RoVi spectra) of the gas phase CO band (cf. black spectrum in **Error! Reference source not found.**). The envelope of minima of the RoVi spectrum (blue in **Figure 2**) corresponds to the spectrum without gas phase CO, which allows a clearer view on adsorbed species under reaction conditions that do not show a rotational fine spectrum. If a lower resolution is employed, the RoVi spectrum of gas phase CO appears as two broad bands (cf. red spectrum in **Error! Reference source not found.**) which overlap with the bands of adsorbed CO, thus impeding to resolve adsorbed species (cf. red spectrum in **Error! Reference source not found.**). In CO oxidation experiments the heat of reaction can cause the normalized spectra to be skewed. This is due to the temperature rising more quickly during the spectrum being recorded under reaction conditions (induced by the evolved heat of reaction) than during recording of the background spectrum. This causes a mismatch between background spectrum and reaction condition spectrum. In these cases a linear baseline is subtracted for better visibility of the data.

TEM of IrO₂@TiO₂

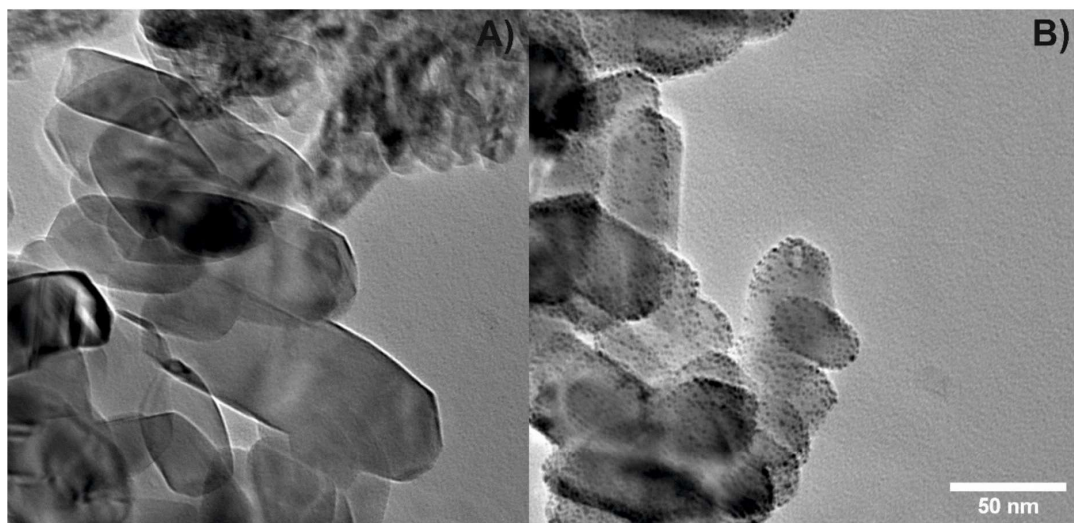


Figure S4. TEM image of A) the pure TiO₂ support and B) IrO₂@TiO₂ at magnification of 81000. The large particles are the TiO₂ support. The dark spots in B) are IrO₂ supported on TiO₂.

XP spectra of incomplete reduction of IrO₂@TiO₂ with H₂

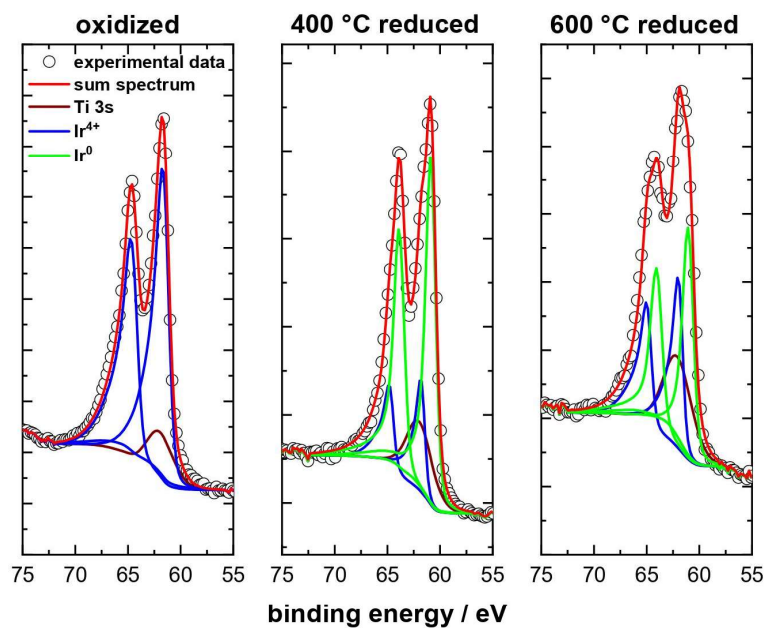


Figure S5. Ir 4f XP spectra of oxidized and reduced IrO₂. The reduced samples were held under the denoted temperature for 24 h.

Raman of Ir⁰ before and after reducing CO oxidation conditions

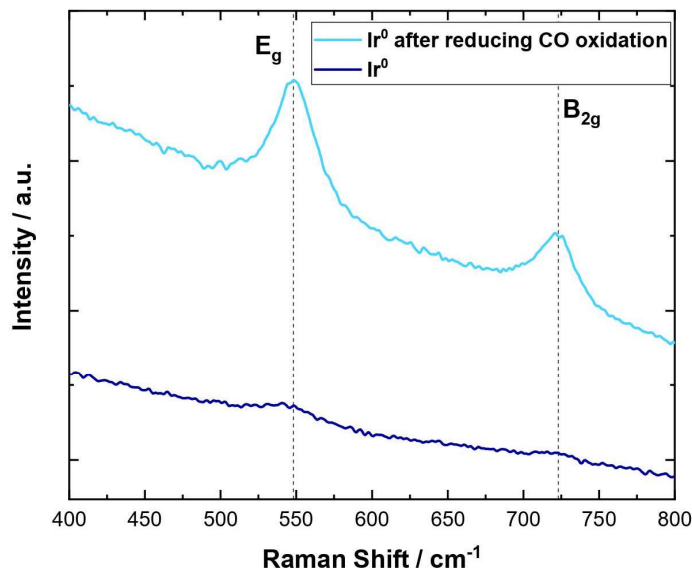


Figure S6. Raman spectra of Ir⁰ before and under reducing (1% O₂/4% CO/95% Ar) reaction feed. One can clearly see the increase of the E_g and B_{2g} bands of IrO₂, demonstrating the oxidation of Ir⁰ under these conditions.

XPS fit parameter and IrO₂@TiO₂ reduction attempts

Table S1. XPS fit parameters.

<i>Species</i>	<i>Peak</i>	<i>Binding energy</i>	<i>FWHM</i>	<i>Fitting parameters</i>
Ir	4f _{7/2}	60.8	1.03	LF(0.6,1,150,300)
	4f _{5/2}	63.8	1.03	LF(0.6,1,150,300)
IrO ₂	4f _{7/2}	61.5	1.30	LF(0.3,1,65,300)
	4f _{5/2}	64.5	1.47	LF(0.3,1,65,300)
TiO ₂	3s	61.9	3.04	GL(30)

The Ir⁰ signal seems to be less after pretreatment at 600 °C, relative to pretreatment at 400 °C. We suspect that at these temperatures the Ir-particles are either overgrown by TiO₂, due to SMSI and/or form a mixed Ir-Ti oxide. We have however not investigated this further.

Blank DRIFT Spectra of rutile-TiO₂ without active component

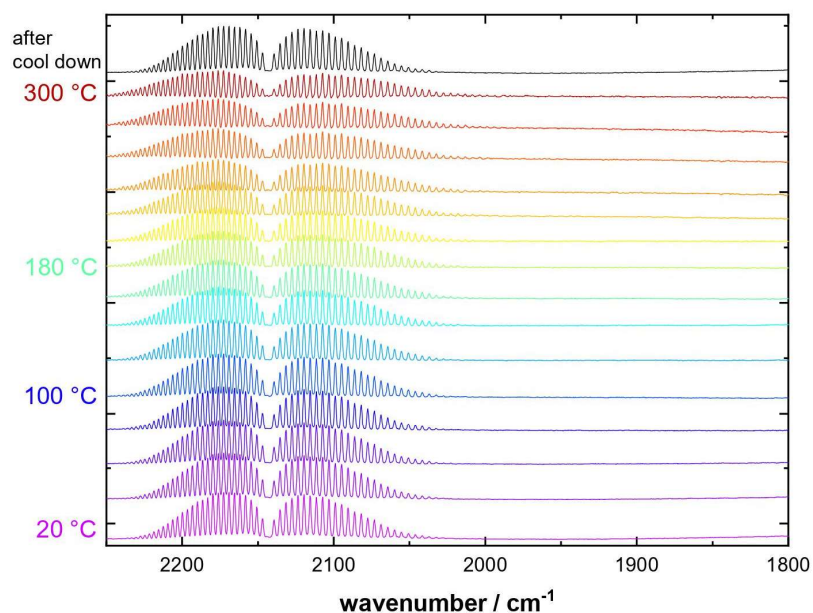


Figure S7. DRIFT spectra of pre-oxidized TiO₂ heated in a CO atmosphere. CO adsorption bands are not observed, while the RoVi fine structure of CO gas appears between 2100-2200 cm⁻¹. The spectrum denoted as “after cool down” was recorded after the sample was cooled back down to room temperature under CO. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

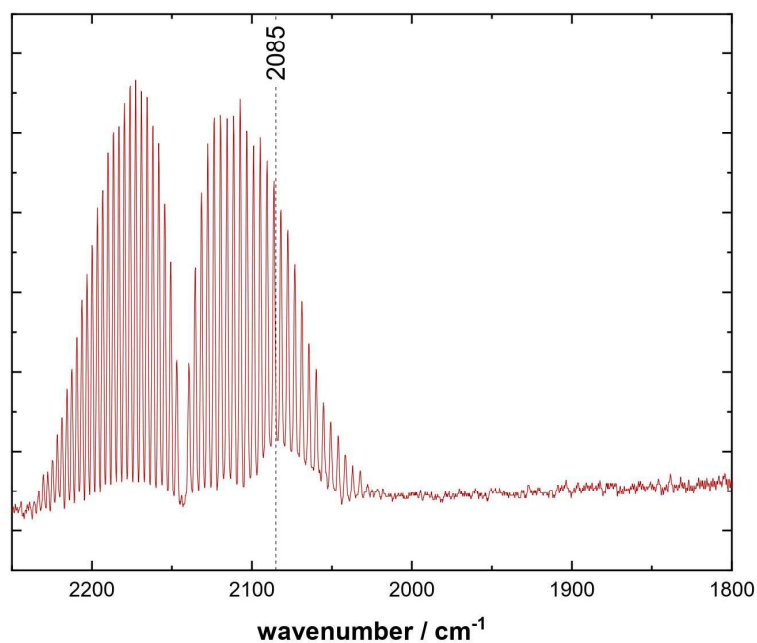


Figure S8. DRIFTS spectrum of CO adsorption on Ir⁰+TiO₂ after oxidative pretreatment under 4% O₂ at 300°C for 12h. As previously shown for IrO₂@TiO₂ only one band without broad shoulder is observed.

5.3 Supporting Information on Publication III

Supporting Information

Active Phase of IrO₂ in the Catalytic CH₄ Combustion Reaction: Operando Infrared Spectroscopy and On-Line Gas Analysis

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2) *Center for Materials Research, Justus Liebig University, Heinrich-Buff-Ring 16,
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* Corresponding author: Herbert.Over@phys.chemie.uni-giessen.de

Table S1: XPS fit parameters.

Species	Peak	Binding energy	FWHM	Fitting parameters
Ir	4f _{7/2}	60.8	1.03	LF(0.6,1,150,300)
	4f _{5/2}	63.8	1.03	LF(0.6,1,150,300)
IrO ₂	4f _{7/2}	61.5	1.30	LF(0.3,1,65,300)
	4f _{5/2}	64.5	1.47	LF(0.3,1,65,300)
TiO ₂	3s	61.9	3.04	GL(30)

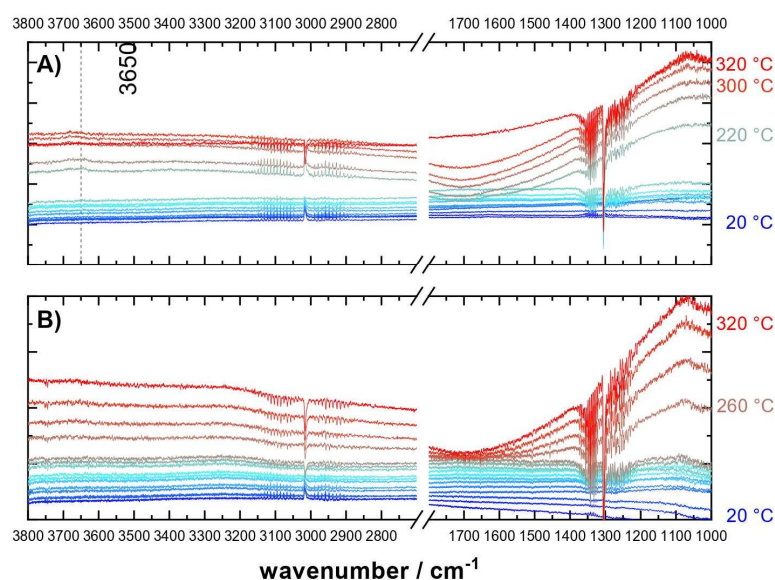


Figure S1: Operando DRIFTS spectra of A) ox-IrO₂@TiO₂ as well as B) red-IrO₂@TiO₂ under 4% CH₄ in Ar. The wavenumber range previously omitted is shown. No additional bands of surface adsorbates can be seen, except possibly some faint features of OH species around 3650 cm⁻¹. The RoVi bands around 3050 cm⁻¹ and 1300 cm⁻¹ correspond to gas phase CH₄. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

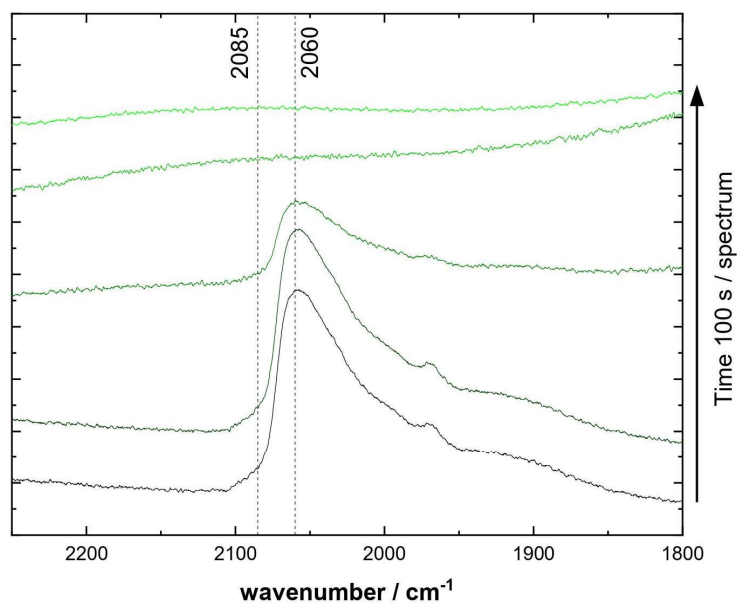


Figure S2: Operando DRIFTS spectra of red-IrO₂@TiO₂ under oxidizing feed composition at 340 °C. The surface CO species are removed indicating an oxidation of the catalyst.

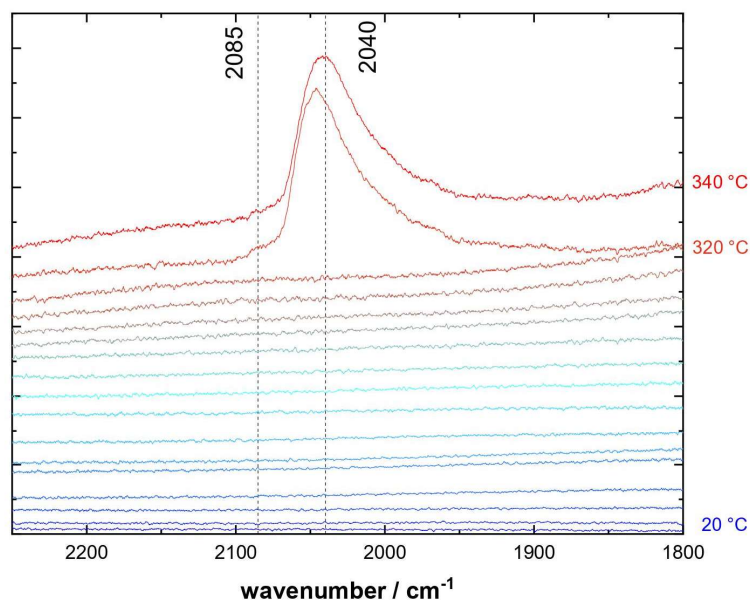


Figure S3: Operando DRIFTS spectra of ox-IrO₂@TiO₂ under reducing feed composition during second reaction cycle. The high wavenumber signal of 2085 cm⁻¹ can now be observed.

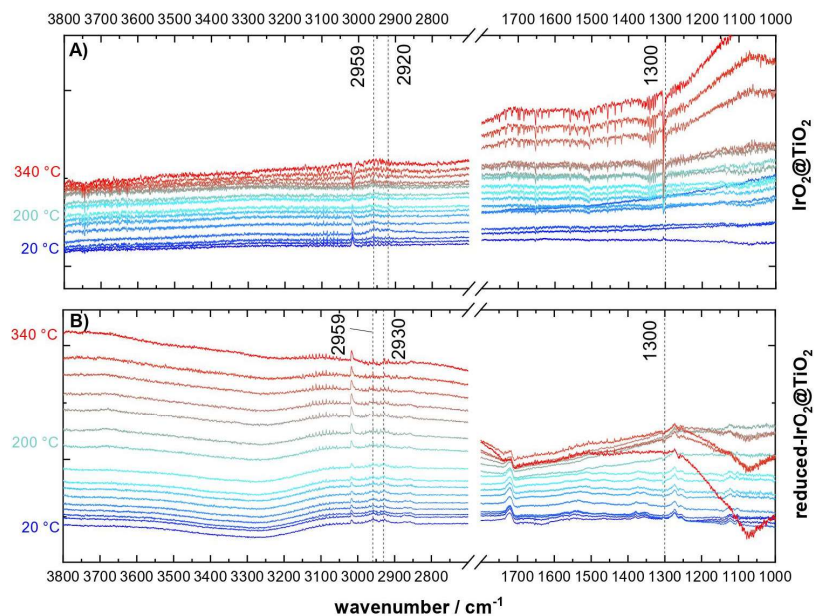


Figure S4: Operando DRIFTS spectra of A) ox-IrO₂@TiO₂ as well as B) red-IrO₂@TiO₂ under oxidizing reaction feed. The wavenumber range previously omitted is shown. Some additional surface species can be seen. The bands around 2940 cm⁻¹ are likely ascribed to formates, the ones below 1750 cm⁻¹ are likely due to carbonate species. The RoVi bands around 3050 cm⁻¹ and 1300 cm⁻¹ correspond to gas phase CH₄. Temperature increment between consecutive spectra is 20 °C. The heating ramp is 1.8 K·min⁻¹.

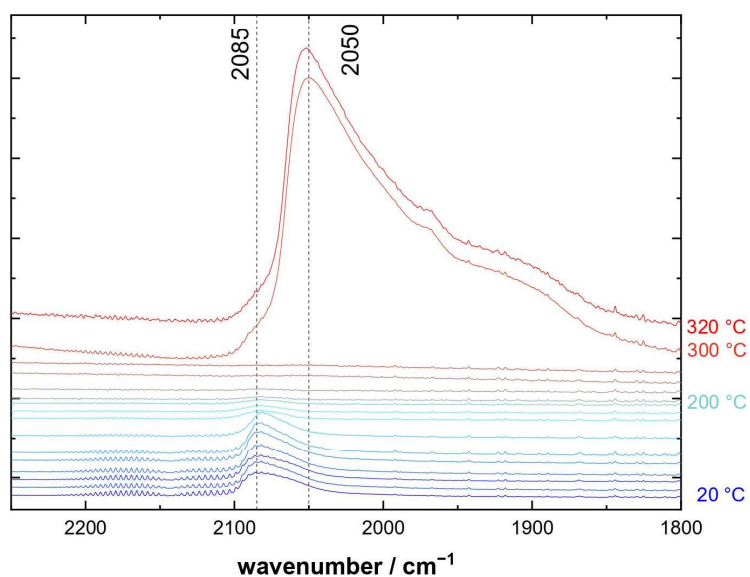


Figure S5: Operando DRIFT spectra of red-IrO₂@TiO₂ during cool down under reducing conditions with addition of CO (1% CH₄ / 1% O₂ / 1% CO / 97 % Ar). The 2085 cm⁻¹ band reemerges with decreasing temperature. Temperature increment between consecutive spectra is 20 °C. The cooling ramp is 1.8 K·min⁻¹.

To verify the presence of the 2085 cm⁻¹ band 1% CO was added to the reaction feed during cool down. DRIFTS spectra are shown in **Figure S4**. Here it can be seen that the 2085 cm⁻¹ band remains visible below the temperature where CO creation from methane is expected. Only in the temperature range from 280°C to 200 °C CO cannot be observed, since CO oxidation by O₂ is faster than the formation by methane activation.

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