Oxidation and Reduction of Ir(100) Studied by High-Energy Surface X-ray Diffraction

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ABSTRACT: The oxidation and reduction of an Ir(100) surface using 2.5, 5, and 10 mbar O2 partial pressure and a sample temperature of 775 K have been studied by using high-energy surface X-ray diffraction (HESXRD) which allowed to record large volumes of reciprocal space in short time periods. The complex 3D diffraction patterns could be disentangled in a stepwise procedure. For the 2.5 mbar experiment the measurements indicate the formation of an Ir(100)-O c(2 × 2) oxygen superstructure along with the onset of epitaxial IrO2(110) bulk oxide formation. For the 5 and 10 mbar O2 partial pressures the formation of additional IrO2 bulk oxide epitaxies with (100) and (101) orientations as well as of polycrystalline IrO2 was observed. Upon CO reduction, we found the IrO2 islands to be reduced into epitaxial and metallic Ir(111) and (221) oriented islands.

INTRODUCTION

The interaction of oxygen with the Ir(100) surface has been investigated in great detail during the past few decades due to the importance of Ir as an oxidation catalyst.1–5 These earlier investigations have been limited to chemisorbed oxygen formed under UHV-like conditions. Recently, however, it was observed that an epitaxial rutile IrO2(110) film may form on the Ir(100) surface at significantly higher oxygen exposures and that this surface has the ability to dissociate and activate methane (CH4) at surprisingly low temperatures.6 Because alkane C–H bonds are among the least reactive known, no process for direct conversion of CH4 into methanol has so far been developed; hence, the facile CH4 dissociation occurring even at liquid nitrogen temperatures on the IrO2(110) surface could have importance for the development of novel and efficient methanol to methane conversion catalysts.7–10 The IrO2(110) surface has a structure similar to the ones of RuO2(110)11 and PdO(101) exposing coordinatively unsaturated sites (CUS) at which catalytic reactions happen,7–10 and the CUS sites at the IrO2(110) surface were also found to be the active sites for the CH4 dissociation.11

However, it has also been reported that the IrO2 did not only show a (110) orientation when forming on the Ir(100) surface but that other IrO2 surface orientations coexisted12 similar to the oxidation of Ir(111)13 at higher O2 pressures. The observation of mixed IrO2 orientations is important, since it may limit the use of IrO2(110)/Ir(100) as a model catalyst. Not surprisingly, IrO2(110) surfaces with much improved surface order have been grown on both TiO2(110) and RuO2(110)/Ru(0001) as templates,14,15 ensuring a single surface orientation, significantly simplifying the understanding of surface reactions on the IrO2(110) surface. In addition to the inconclusiveness concerning the coexistence of various IrO2 phases on the surface, also the dynamics of their formation is as of today still unclear. Hence, a recent time-lapsed ambient pressure X-ray photoelectron spectroscopy study concluded a rapid and autocatalytic growth mechanism that, however, only occurs after a long induction period with constant oxygen coverage.16 These findings make a detailed investigation of the oxidation dynamics of the Ir(100) surface necessary, also with the goal to identify conditions that stabilize the formation of desired IrO2 orientations.

In this contribution, we discuss the results of a time-resolved high-energy surface X-ray diffraction (HESXRD) investigation of the structural changes of an Ir(100) surface during oxidation and reduction using O2 partial pressures of 2.5, 5, and 10 mbar at a temperature of 775 K and a constant total pressure of 500 mbar. At 2.5 mbar oxygen partial pressure we detected the appearance of an oxygen Ir(100)-O c(2 × 2)
superstructure and the onset of the formation of an epitaxial IrO$_2$(110) bulk oxide. Upon oxidation at 5 and 10 mbar of O$_2$ we found the formation of additional (100) and (101) orientated epitaxial IrO$_2$ bulk oxides as well as the appearance of polycrystalline IrO$_2$, introducing defects which may also affect the surface chemical properties. The HESXRD approach demonstrates its applicability to disentangle a complex diffraction pattern with a large number of diffraction spots and rings. When reducing the 10 mbar oxidized IrO$_2$/Ir surface with 5 mbar CO partial pressure, epitaxial (111) and (221) oriented metallic islands were observed to form in the oxide, similar to what has been observed for the reduction of PdO(101).18,35

EXPERIMENTAL SECTION

Sample and Experimental Setup. As sample we used a round, hat-shaped Ir(100) single crystal model catalyst (Surface Preparation Lab (SPL)). Its polished surface featured a circular diameter of 6 mm. The crystal was cleaned by cycles of Ar$^+$ sputtering at 1.5 keV acceleration voltage, 10 mA emission current, and 2 × 10$^{-5}$ mbar Ar pressure at room temperature (RT), followed by UHV annealing at 1100 K. The observation of narrow and intense crystal truncation rod (CTR) signals after the sputtering/annealing cycles indicated a clean and unreconstructed Ir surface with large (100) terraces.

As sample environment a dedicated in situ catalysis reactor chamber was used in which the Be dome ambient pressure reactor part can be sealed from the UHV dedicated part of the chamber. Its schematics are shown in Figure 1a. It allows for a
UHV preparation of the sample surface as well as operando catalysis studies in the sealed reactor cell.

The gas system connected to the reactor cell provides a computer-controlled introduction of gases, as it is equipped with individual mass flow controllers for each gas and a back-pressure controller downstream the cell outlet regulating the cell pressure. The gas composition inside the cell is constantly being probed by leaking gas into the UHV part where the mass spectrometer (MS) is situated. As gases we used diluted O₂ (10% O₂ in 90% Ar), diluted CO (10% CO in 90% Ar), and pure Ar (carrier gas), all at 5 N purity. The use of a carbonyl trap, located in the CO gas line upstream of the reactor cell, guaranteed the cleanliness of the CO gas mixture entering the reactor.

High-Energy Surface X-ray Diffraction. The experiment was performed at Petra III, Deutsches Elekronen-Synchrotron (DESY) in Hamburg, Germany, in experimental hutch 2 (EH2) of the High Energy Materials Science Beamline P07.20

A photon energy of 71 keV was used in the experiments, with a photon flux of ~5 × 10¹⁰ photons/s. The incident angle of the X-ray beam was set to 0.06°, which is below the critical angle of Ir at 71 keV (α₉₀° = 0.084°), to enhance the surface signal compared to diffraction signals from the bulk. Because the bulk Bragg reflections are many orders of magnitude stronger than the surface signal, tungsten beamstops were used on the detector to block the corresponding signals and avoid detector damage. These beamstoppers consequently left corresponding circular shadows clearly visible on the detector images. Moreover, the direct beam was blocked by using a Ta beamstop behind the Be dome. An additional Ta mask was used to block the scattered signals created by the entrance and the exit of the X-ray beam at the Be dome.17

As detector a PerkinElmer flat-panel X-ray detector was used, especially suited for X-ray photon energies higher than 20 keV. The detector features an active area of 410 × 410 mm², with a pixel size of 200 × 200 μm² and a total resolution of 4 MP.

The sample surface was first aligned with the help of an X-ray eye located inside the experimental hutch behind the sample position. Thereafter, the sample’s height alignment was finalized by optimizing the signal intensity on an Ir(100) CTR using the 2D detector. The latter fine adjustment was repeated before each measurement.

Data Acquisition and Analysis Procedures. For the HESXRD data acquisition two distinct measurement modes were employed.17,21,22 (1) Timescans during which, with a stationary sample, 2D images were acquired in a distinct reciprocal space plane of interest and with a high temporal resolution up to 5 Hz. (2) Rotational scans during which the sample was rotated around its surface normal while 2D images were acquired with an angular resolution of 0.1°, covering 100° of reciprocal space with a total acquisition time of 260 s. Schematic representations of these two data acquisition modes and of the successive data processing are shown in Figure 1b–g and will be elucidated in the following.

Figure 1b illustrates the acquisition of timescans, which we employed when changing the gas flow composition to qualitatively track structural changes of the Ir(100) surface such as the appearance or disappearance of transient oxide structures. Figure 1c, in turn, depicts the principle of the acquisition of rotational scans, which we acquired under stable experimental conditions. Rotational scans provide a 3D data set of reciprocal space containing all structural information and ensuring that no crystalline structural phases are being missed under the set conditions.

Figures 1d and 1e–g then illustrate how the data obtained from timescans or rotational scans can be processed further. Hence, in the case of timescans (Figure 1b), the plotting of the integrated intensities of defined regions of interest (ROIs) allows the tracking of the surface structural transitions as a function of time, as is depicted in Figure 1d.

The data extracted from rotational scans can be plotted in three different ways, which are illustrated in Figure 1e–g. Figure 1e displays the first possible data representation, in which for each detector pixel the highest intensity value probed during the full rotational scan (and thus the value which corresponds to the best alignment for this reciprocal space point) is plotted, thereby projecting the 3D reciprocal space onto a 2D out-of-plane image. Similarly, the rotational scan data shown in Figure 1f consist of the projection of the integrated intensity per pixel onto the HK plane, resulting in an in-plane projection of the data in a LEED-like manner. The latter allows the deduction of the epitaxial relationships between structural phases and the Ir(100) surface. Finally, Figure 1g shows an example of a pole figure. To obtain these, the diffraction signals that lie within a hemisphere centered around a reciprocal space vector Q₀ with a thickness of ΔQ obtained from the 3D rotational scan data (as indicated in Figure 1c) were identified and simulated using a Rietveld analysis approach. The simulated diffraction data were then projected onto a 2D plane by using polar coordinates (see Supplementary Note 1 and Figure S1 in the Supporting Information). This way of data illustration allows to isolate the diffraction signals of certain Q₀ values from others, thereby enhancing the visibility of the diffraction features of interest. To identify the diffraction signals within such a hemisphere, only the diffraction features that matched the positions of IrO₂ crystallographic families were integrated, taking a C₁ rotational symmetry into account.

To describe the structure of the Ir(100) single crystal, a set of tetragonal basis vectors (a₁, a₂, a₃) was used, with a₁ and a₂ lying in the surface plane and a₃ perpendicular to them. The length of a₁ and a₂ constitutes a₀/√2 and corresponds to the atomic nearest-neighbor distance in the Ir(100) surface plane. The length of the out-of-plane vector a₃ corresponds to a₀, where a₀(Ir) = 3.839 Å. All (H, K, L) values used in the HESXRD data refer to this basis vector set.

**RESULTS**

In the following, the surface structural changes of the Ir(100) surface during in situ oxidation and reduction will be discussed. The experiment was performed at a sample temperature of 775 K and a total reactor pressure of 500 mbar, where Ar was used as carrier gas and to top up to the constant total gas flow of 50 mL/min. The timelines of the experiment along with the individual gas signals measured by mass spectrometry are shown in Figures S2–S4 and consisted of two consecutive cycles of in situ oxidation and one CO reduction cycle in between. Additional information about the experimental outline can be found in Supplementary Note 2.

Because we found the overall structural changes of the Ir(100) surface during the two oxidation cycles to show the same tendencies, we will focus on the findings of the second oxidation cycle as the oxide diffraction signals appeared at an earlier stage compared to the first cycle. This we ascribe to an additional cleaning effect by the first oxidation/reduction cycle.
on the metal surface as well as to metallic islands that persisted on the Ir(100) surface after the first oxidation, which may act as nucleation centers and promote oxide formation.

**Time-Resolved In Situ Oxidation Study.** During the *in situ* experiment the sample temperature was kept at 775 K. The cycle started with reducing conditions under CO (condition i: 5 mbar CO, 45 mbar Ar) to ensure a reduced surface prior to the oxidation, followed by exposure to pure Ar flow (condition ii: 50 mbar Ar). The subsequent in situ oxidation was performed by the stepwise increase of the partial O2 pressure from 2.5 mbar (condition iii: 2.5 mbar O2, 47.5 mbar Ar) to 5 mbar (condition iv: 5 mbar O2, 45 mbar Ar) and 10 mbar (condition v: 10 mbar O2, 40 mbar Ar).

**Figure 2.** 2D diffraction patterns obtained from rotational scans by displaying for each pixel the highest intensity value measured during the rotation for (a) the reduced Ir(100) surface measured under pure Ar flow, (b) 2.5 mbar O2 partial pressure, (c) 5 mbar O2 partial pressure, and (d) 10 mbar O2 partial pressure, all measured during the second oxidation cycle.

**Figure 3.** (a) Two summed images extracted from the rotational scan measured at an O2 partial pressure of 2.5 mbar (second oxidation cycle) that enhance the visibility of the superstructure rods at (0.5, 0.5) and (0.5, 1.5) indicated by white ellipses. (b) In-plane representation of the same rotational scan as in (a), where the positions of the superstructure rods and of the Ir(100) CTRs are indicated by open red and blue circles, respectively. The two frames summed in (a) are indicated by the gray arrows and the white dashed lines. (c) Top view of expected rod positions for a c(2 × 2) superstructure (red dots and yellow unit cell) on a (100) surface (blue circles and yellow unit cell). (d) Top view of the ball model of the Ir(100)-O c(2 × 2) structure with the O atoms located at bridge sites. The latter have been concluded to be the most stable sites for the Ir(100)-O c(2 × 2) structure.
Every time we switched the gas composition toward higher O₂ partial pressures, we performed timescans in a reciprocal space plane sensitive to the (10L) CTR of the Ir(100) surface to track potential surface structural changes. Once the gas flows of the set experimental condition had stabilized (about 30 min into the set condition), rotational scans were performed to obtain information about the 3D reciprocal space. Summed out-of-plane HESXRD images extracted from the timescans just before and after the gas switches are summarized in Figure S3b. Figure 2a–d in turn shows the rotational scans projected onto a 2D out-of-plane HESXRD image, displaying for every pixel the highest intensity probed during the scan. The corresponding rotational scans of the first oxidation cycle are shown in Figures S4b and S5, the corresponding timescans of the first oxidation cycle are shown in Figure S4b.

Figure 2a shows the rotational scan recorded on the reduced surface under condition i prior to the second oxidation cycle: Along the L-direction crystal truncation rods (CTRs) are clearly discernible, originating from the Ir(100) surface and running through the Ir Bragg peaks. Their visibility, even at the anti-Bragg position between two Ir Bragg peaks, as well as the absence of further diffraction signals, indicate a well-ordered and metallic Ir(100) surface with large terraces prior to its oxidation. It is noteworthy that we did not observe the (5 × 1) reconstruction of the metallic Ir(100) surface that was observed in earlier studies, which could be due to differences in the temperature or the different experimental conditions given by the flow reactor setup of this study.

When switching from pure Ar flow (condition ii) to slightly oxidizing conditions under 2.5 mbar partial O₂ pressure (condition iii), both, the timescans measured during the change in gas composition (Figure S3b) and the rotational scan in Figure 2b measured under stable conditions of 2.5 mbar O₂ revealed the preservation of the Ir(100) CTRs. This implies a conservation of the well-ordered Ir(100) surface under these slightly oxidizing conditions. Moreover, and rather surprisingly, the rotational scan revealed the presence of an ordered superstructure under these conditions, which we concluded from the appearance of superstructure rod signals. Because their signal intensity was found to be rather weak, the superstructure rods cannot directly be deduced from the summed 2D image of the rotational scan shown in Figure 2b. Instead, we extracted two 2D frames from the rotational scan of Figure 2b in which two example superstructure rods are most visible. Their summed image is presented in Figure 3a, with the two superstructure rods located at Q∥(0.5,0.5) and (0.5,1.5) of the Ir surface lattice, respectively. To illustrate their position with respect to the Ir(100) surface lattice, Figure 3b moreover displays the in-plane projection of the rotational scan of Figure 2b, visualizing the diffraction data in a LEED-like manner. Its comparison with Figure 3c, which shows the calculated positions of a c(2 × 2) superstructure with respect to the Ir(100) lattice, implies that the formed superstructure rods belong to an Ir(100)-O c(2 × 2) superstructure, also indexable as (√2 × √2)R45°-O. As the rods are located in other reciprocal space planes than the one probed in the timescan, their appearance could not be followed as a function of time.

The formation of an Ir(100)-O c(2 × 2) superstructure has, to our knowledge, experimentally not yet been observed. Moreover, in various density functional theory (DFT) calculations, the formation of a p(2 × 1)-O overlayer phase for an oxygen coverage of 0.5 ML has been concluded to be energetically more favorable compared to the c(2 × 2) overlayer. Yet, for a flow reactor cell as used in this study, different boundary conditions than the ones presumed in the DFT calculations may apply. With regard to the different possible adsorption positions for the oxygen atoms on the Ir(100) surface it has been found that the bridge site is most favorable. Figure 3d shows that the top view of a ball model of the Ir(100)-O c(2 × 2) overlayer with the oxygen atoms adsorbed on bridge sites and thus of the structural phase that most likely explains our experimental findings. Yet, it has to be mentioned that it is surprising to detect the scattering signal from a 0.5 ML oxygen structure as the scattering intensity scales with Z² of the scattering atom, where Z corresponds to the atomic number and is accordingly expected to be extremely weak for an oxygen chemisorption. Thus, it is likely that the Ir(100) surface is corrugated and the heavy Ir atoms contribute to the scattering.

Finally, it is striking that the rotational scan measured under 2.5 mbar of O₂ and unlike the timescan in the transition from Ar flow to 2.5 mbar of O₂ shows a faint, yet well-discernable diffraction peak at Q∥ = 3.96 Å⁻¹ on the specular rod at H = K = 0, which can be traced back to the formation of (110)-oriented IrO₂ bulk oxide islands and, accordingly, mark the onset of bulk oxide formation. Thus, our data suggest that once the gas flows have stabilized (about 25 min into the set conditions), the Ir(100) surface exhibits a coexistence of small (110)-oriented IrO₂ islands and the Ir(100)-O c(2 × 2) overlayer phase.

During the next oxidation step, when increasing the O₂ partial pressure from 2.5 to 5 mbar of O₂ (condition iv), the timescan (Figure S3b) revealed that the diffraction signals belonging to the (110)-oriented IrO₂ islands grew more intense; at the same time, more diffraction peaks appeared that can also be ascribed to the IrO₂(110) phase. This implies that the IrO₂ islands grew larger in size, and their coverage increased. At the same time, the timescan revealed that the IrO₂(110) diffraction peaks progressively smeared out in a radial direction, implying a gradual tilting of the IrO₂(110) islands with respect to the sample surface normal, as we have described earlier and which is also elucidated in Supplementary Note 3 and in Figure S6 of the Supporting Information. By the end of the timescan, about 15 min into the set condition of 5 mbar of O₂, the tilt angle comprised around ±18° with respect to the sample surface normal, suggesting a corresponding tilt of the bulk oxide islands with respect to the sample surface normal.

While the timescan performed at 5 mbar O₂ partial pressure contained diffraction peaks that can only be ascribed to IrO₂(110) islands, the corresponding rotational scan, displayed in Figure 2c and acquired only about 2 min later, revealed a multitude of diffraction peaks that cannot solely be ascribed to the IrO₂(110) orientation. As will be explained more thoroughly in the next section, the peak pattern can instead be explained by the coexistence of (110)-, (101)-, and (100)-oriented IrO₂ bulk oxide islands. This delayed oxidation of the Ir(100) surface, which in general requires either elevated O₂ pressures or aggressive oxidants to be oxidized, is in line with the findings of a recent ambient pressure X-ray photoelectron spectroscopy investigation on the oxidation of Ir(100), which concluded, only after a long waiting period under O₂ exposure, the sudden and rapid formation of IrO₂ bulk oxide via an autocatalytic growth mechanism. Moreover, it is interesting to
note that the Ir(100) CTRs upon the formation of these coexisting bulk oxide structures greatly decreased in intensity, signaling a roughening of the Ir(100) surface upon bulk oxide formation. Finally, it should be noted that the first oxidation cycle revealed the same tendencies of bulk oxide formation, yet the bulk oxide diffraction peaks were found to be much weaker compared to the ones of the second oxidation cycle (see Figure S5). On the one hand, this can be traced back to the delayed oxide formation for the reasons discussed above. Yet, it is also noteworthy that the CO signal (see Figures S2 and S4) was still high, probably resulting in a slightly reducing atmosphere that impeded bulk oxide formation.

When increasing the partial O2 pressure further to 10 mbar of O2 (condition υ), no further oxide diffraction peaks appeared. For the second oxidation cycle discussed here, we even found the intensity of the bulk oxide peaks to slightly decrease in intensity, as can be inferred from the rotational scan shown in Figure 2d. Yet, we ascribe this decrease in intensity to experimental problems in our O2 gas feed, which can also be deduced from the O2 signal shown in Figures S2 and S3. In contrast, the first oxidation cycle, in which we were not facing any gas feed problems, revealed a steady increase in the IrO2 Bragg peak intensities, signaling the further oxidation of the Ir(100) surface and the ongoing growth of the (110)-, (101)-, and (100)-oriented bulk IrO2 islands (see Figure S5).

In this respect it is moreover noteworthy that, especially under 10 mbar O2 partial pressure, the IrO2 diffraction peaks smeared out even more along the radial direction, implying a progressive tilting of the bulk oxide islands with respect to the sample surface normal. The intensity increase of the Debye–Scherrer rings suggests the progressive appearance of polycrystalline IrO2 phases.

Identification and Quantification of the Different IrO2 Phases. In the previous section we discussed the appearance and the temporal evolution of the different IrO2 orientations as a function of the oxygen partial pressure. In the following, we used various data visualizations to disentangle the complex 3D diffraction patterns measured at 5 and 10 mbar O2 partial pressure with the aim to identify the diffraction peaks and to ascribe them to different IrO2 orientations. This not only provided quantitative information about the IrO2 islands but yielded also insight into the epitaxial relationship of the different IrO2 bulk oxide orientations with respect to the Ir(100) surface.

One way to visualize and identify the diffraction peaks of the different IrO2 orientations is indicated in Figure 4, which shows the 2D diffraction pattern deduced from the rotational scan measured at 10 mbar O2 partial pressure. Therein, the Ql values for which diffraction peaks from (110)-, (101)-, and (100)-oriented IrO2 bulk oxides can be expected are indicated by respectively colored dashed horizontal lines in orange, purple, and red. The Ql values of the horizontal dashed lines are given by the lattice plane distances of the different IrO2 orientations perpendicular to the sample surface and accordingly act as a fingerprint for the latter. The Bragg peaks of the corresponding bulk oxides are indicated in the same color by open circles, where their radius scales with the expected Bragg peak intensities. With Figure 4 being a rotational scan that covers 100° of rotation angle around the surface normal and thus contains the full reciprocal space information, it becomes evident that the oxidized surface under 5 and 10 mbar O2 pressures can be fully explained by the coexistence of (110)-, (101)-, and (100)-oriented IrO2 bulk oxides.

To obtain information about the epitaxial relationship of the IrO2 bulk oxide orientations with respect to the Ir(100) surface, three in-plane maps (HK plane) were extracted at the six Ql values, adding two maps for each epitaxy (Ql = 3.96 1/Å plus Ql = 5.93 1/Å for IrO2(110), Ql = 2.84 1/Å plus Ql = 5.49 1/Å for IrO2(101)), and Ql = 1.67 1/Å plus Ql = 4.86 1/Å for IrO2(100)), each of which contains the Bragg peaks of one IrO2 orientation. They are shown in Figure S7b for the (110)-, (101)-, and (100)-oriented IrO2 bulk oxides, respectively, with their corresponding in-plane reciprocal unit cells. The rocking scans deduced from ROIs of selected IrO2 Bragg peaks are shown in Figure S8. The unit cells’ orientation with respect to the Ir(100) lattice reveals that the diffraction peaks related to the (110) planes in Figure S7b can be explained by four rotational domains of IrO2(110)R27°, rotated by 27° with respect to the Ir(100) substrate lattice. The diffraction peaks of the IrO2(101) and the IrO2(100) bulk oxides in Figure S7b, in turn, can in each case be ascribed to two domains, rotated by 90° with respect to each other, both aligned along the Ir(100) substrate lattice.

These findings are in good agreement with our pole figure interpretation. Figure 5a shows the pole figures for the hemispheres centered around three Ql values that correspond to three of the six dashed Ql values (Ql = 3.96 1/Å, Ql = 4.86 1/Å, and Ql = 5.93 1/Å) in Figure 4 that were used for the in-plane maps in Figure S7. As can be deduced from Figure 5a, each pole figure contains diffraction peaks from all three IrO2 orientations. Their positions with respect to each other and with respect to the Ir(100) lattice confirms the presence of four rotational domains of IrO2(110)R27° and two domains of the IrO2(101) and the IrO2(100) bulk oxides aligned with the Ir(100) lattice. On the basis of these findings, we summarized the epitaxial relationships of the IrO2 bulk oxide structures (one domain in each case shown) and their orientation with respect to the Ir(100) surface. The bottom panels in Figure 5b show the corresponding ball model side views of the three different IrO2 orientations.

**Figure 4.** Rotational scan measured under 10 mbar O2 partial pressure (first oxidation cycle) and projected onto a 2D image by displaying the highest intensity measured for each pixel during the scan. The diffraction peaks stemming from the (110)-, (101)-, and (100)-oriented IrO2 bulk oxides are indicated by orange, purple, and red open circles, respectively. The horizontal dashed lines indicate the values Ql = 1.67 1/Å, Ql = 2.84 1/Å, Ql = 3.96 1/Å, Ql = 4.86 1/Å, Ql = 5.49 1/Å, and Ql = 5.93 1/Å, for which the in-plane maps in Figure S7 were deduced.
Our experimental findings are partly in line with a recent investigation combining low-energy electron diffraction (LEED) and temperature-programmed desorption (TPD).\textsuperscript{12} It concluded a variety of bulk oxide structures in the pressure range between 0.05 and 5 Torr, including a commensurate IrO$_2$(101) structure in an oxygen pressure range up to 0.2 Torr, a commensurate IrO$_2$(110)\textsuperscript{R27°} structure for oxygen pressures between 0.5 and 1 Torr, and an IrO$_2$(110) epitaxy aligned with the Ir(100) lattice that replaces the IrO$_2$(110)\textsuperscript{R27°} structure at higher oxygen pressures of 5 Torr. While our data also contain clear evidence of an IrO$_2$(110)\textsuperscript{R27°} structure, diffraction signals from an IrO$_2$(110) structure that is aligned with the Ir(100) surface are missing, even under 10 mbar O$_2$ partial pressure. Note, however, that different experimental conditions were employed in our studies (flow reactor cell, higher total pressure of 500 mbar), which could shift the occurrence of oxide structures to higher temperatures or oxygen partial pressures.

Because of the conflicting conclusions that exist in the literature with respect to the structures that are present on the oxidized Ir(100) surface, it is of great interest to quantify the respective amounts of the different IrO$_2$ orientations as a function of the probed oxygen partial pressures. We determined the relative amounts of the different IrO$_2$ epitaxies by comparing the integrated peak intensities of the different IrO$_2$ orientations. They were deduced from a rotational scan using the ROIs indicated in Figure S7a, where the intensity as a function of the rotational angle are shown for the first and second oxidation cycle in Figures S8 and S9, respectively. The results for cycle 1 and cycle 2 are summarized in Table 1, and the data reveal that in the probed conditions the IrO$_2$(101) epitaxy always predominates, coexisting with smaller amounts of the IrO$_2$(100) and IrO$_2$(110) epitaxies. It is moreover noteworthy that the highest percentage of around 30% of the IrO$_2$(110) epitaxy, which has earlier been attributed to facilitate the splitting of the CH$_4$ molecule at low temperatures,\textsuperscript{6} has been found at 5 mbar partial oxygen pressure under the first oxidation cycle. This finding indicates that rather moderate oxidation conditions may stabilize the presence of this particular IrO$_2$ orientation.

It is moreover striking that we find the individual bulk oxide epitaxies to feature only small angular distributions (in-plane mosaicity) with respect to their preferred unit cell alignment. Table 1 summarizes the angular distributions of the different

![Figure 5](https://doi.org/10.1021/acscpc.1c10250)
epitaxies, given as full width at half-maximum (FWHM) with respect to the preferred direction. They were obtained from the rotational scans measured at 5 and 10 mbar O₂ partial pressures by using the ROIs highlighted in Figure S7a and are also shown as scans in Figures S8 and S9.

| Table 1. Relative Percentages (“rel perc”) and Bragg Peak FWHMs (“FWHM”) of the Three Different IrO₂ Epitaxies as a Function of the Probed Condition for Both Cycle 1 and Cycle 2 |
|---------------------------------|-----------|-----------|-----------|-----------|-----------|-----------|
|                                  | cycle 1   | cycle 1   | cycle 2   | cycle 2   |           |           |
|                                  | 5 mbar    | 10 mbar   | 5 mbar    | 10 mbar   |           |           |
| [100] rel perc:                 | 12.7%     | 16.47%    | rel perc: | 7.59%     | tot int:  | 19.23%    |
| FWHM = 1.9°                     |           |           | FWHM = 1.5° | FWHM = 2.2° | FWHM = 2.3° |
| [110] rel perc:                 | 29.30%    | 14.58%    | rel perc: | 3.77%     | rel perc: | 6.58%     |
| FWHM = 2.8°                     |           |           | FWHM = 2.5° | FWHM = 3.2° | FWHM = 3.3° |
| [101] rel perc:                 | 57.94%    | 68.93%    | rel perc: | 88.62%    | rel perc: | 74.18%    |
| FWHM = 1.9°                     |           |           | FWHM = 1.7° | FWHM = 1.4° | FWHM = 1.5° |

Tracking the Surface Structural Changes during the Reduction of the IrO₂ Islands. In the previous section the structure of the oxidized Ir(100) surface was discussed. In the following we will turn to the structural changes the oxidized Ir(100) surface underwent upon reduction in CO.

To investigate the stability of the IrO₂ bulk oxides and to track the surface structural changes of the fully oxidized surface under reducing conditions, we performed timescans with a temporal resolution of 0.2 s aligned to the reciprocal space plane containing the (10L) CTR of the Ir(100) surface while changing the gas composition from 10 mbar O₂ partial pressure (condition v) to 5 mbar CO partial pressure (condition i). Also during this experiment, which was performed after the first oxidation cycle (see timeline in Figure S2), as for all the previous experiments, the temperature and total pressure were kept constant at 775 K and 500 mbar, respectively.

Figures 6a and 6b show the 2D images obtained from the rotational scans measured on the initially fully oxidized sample (a: condition v), and the subsequently reduced sample (b: condition i), where distinct regions of interest (ROIs) of the
bulk oxide and the metallic structures are indicated by colored squares. Figure 6c displays the temporal development of the integrated intensities of these ROIs as deduced from the aforementioned timescan when switching from oxidizing to reducing conditions. The left of Figure 6c shows the entire timeline of the time-resolved experiment, while the right side shows a zoom-in onto the first ∼40 s of the reduction.

It was at time 0 s that the gas environment was changed from 10 mbar O₂ partial pressure to 5 mbar CO partial pressure. As can be deduced from Figure 6c, at around time 19 s after this gas switch, the integrated ROI intensities of the IrO₂ epitaxies suddenly dropped, indicating the reduction of the oxide phases. The delay with respect to the gas switch at time 0 s can partially be ascribed to the time it took for the gases to reach the reactor. Once the reduction started, however, it was within only about 2 s that the IrO₂ diffraction signals of all three epitaxies dropped, implying a fast reduction of the oxide islands. The data moreover indicate that IrO₂(110) was the bulk oxide orientation that started being reduced prior to the others.

At the same time as the diffraction signals of the IrO₂ epitaxies disappeared, new diffraction signals emerged (indicated by blue and green boxes in Figure 6a,b). Their positions in reciprocal space can be explained by epitaxial metallic Ir(111) and Ir(221) islands on the IrO₂ islands, resulting on the Ir(100) surface upon complete reduction. Moreover, the Ir(100) CTR suddenly and drastically dropped in intensity upon the gas switch, although it remained visible in the HESXRD pattern also under these reducing conditions. These observations suggest a complete reduction of the IrO₂ islands and their transformation into epitaxial (111)- and (221)-oriented metallic Ir islands, along with a consequent roughening of the Ir(100) surface, similar also to what has previously been observed in the case of PdO.18,35

Subsequently, between 20 and ∼200 s, the Ir(111) and Ir(221) signals decayed while the Ir(100) CTR signal slowly recovered, suggesting a reordering of the sample surface due to thermal annealing. In our observation, a complete recovery of a pristine Ir(100) surface was not possible, and minor Ir(221) refaceting persisted on the crystal even after several cleaning (sputtering and annealing) cycles. This, however, did not appear to have major consequences for the reoxidation of the sample, as the general tendencies of the surface oxidation were found to be the same for the second oxidation cycle. Yet, since the Ir(100) was found to oxidize faster in the second oxidation cycle, the Ir(221) islands could act as nucleation centers for oxide formation, suggesting that the sample’s redox cycling behavior should be investigated in more detail.

To unequivocally determine the epitaxies of the metallic Ir islands that form during reduction, we generated pole figures also for the postoxidation reduced surface. They are shown in Figure 7a and were deduced from the rotational scan acquired after switching to 5 mbar CO partial pressure (condition i). The data can be explained by the presence of four different domains of (111)-oriented islands as well as of two domains of Ir(221) islands rotated by 90° around the surface normal with respect to each other. The left and center panel in Figure 7b show the top view of the ball models for one domain of each
orientation; the right panel in Figure 7b displays the corresponding ball model side views. While the formation of the (111)-oriented metallic Ir islands can be explained by the fact that the close-packed (111) surface has the lowest surface energy of all Ir surfaces and is accordingly energetically most favorable, DFT calculations have indicated that also the Ir(221) surface has a low surface energy compared to other high index facets, which could explain its appearance upon reduction. Moreover, given the estimated surface unit cell length for Ir(221) of 8.11 Å with respect to 2.70 Å of Ir(100), this would fit within 2% strain in the Ir(100) surface atop positions. The low surface energy of the Ir(221) can be traced back to the fact that the high index facet Ir(221) consists of Ir(111) four rows terraces with Ir(111) steps (see Figure 7b). Because of this it is, however, also not possible to disentangle between Ir(221)-oriented islands and tilted Ir(111) islands in the diffraction pattern, suggesting that also the latter could explain some of the diffraction peaks that appeared upon reduction.

Finally, it is noteworthy that after the second in situ oxidation up to 10 mbar O₂ partial pressure, we exposed the oxidized sample to pure Ar flow (condition ii), instead of reducing it with CO, and found the IrO₂ bulk oxides to be stable against decomposition, which could be related to oxygen impurities of the Ar gas and/or the total high pressures of 500 mbar used the experiment. Yet it shows that once formed, the bulk oxides appear to be stable against decomposition under these conditions.

■ DISCUSSION

Despite minor discrepancies, we find the general behavior of the Ir(100) surface to be the same during both oxidation cycles, and we summarized the overall scenario of the surface structural changes for an Ir(100) model catalyst during oxidation and reduction in Figure 8. Thus, already under 2.5 mbar O₂ partial pressure a c(2 × 2)-O superstructure may form that at a later stage under these conditions may coexist with small IrO₂(110) islands, marking the onset of bulk oxide formation. Under 5 and 10 mbar O₂ partial pressure, and also with a significant delay into the set condition, further IrO₂ bulk oxide orientations, namely IrO₂(101) and IrO₂(100), form, which then coexist with the IrO₂(110) bulk oxide. While the different bulk oxide islands increase in size, the IrO₂(101) orientation becomes the clearly dominating orientation under these conditions. It is also under 5 mbar O₂ partial pressure that the surface features an increasing amount of tilted bulk oxide islands along with the emergence of polycrystalline bulk oxide.

Our experiment accordingly shows that multiple IrO₂ phases and epitaxies form, in line with previous studies, and that the number of differently oriented oxides make the Ir(100) difficult to use as a model system to produce well-ordered IrO₂(110) surfaces, in particular when using a flow reactor with added complexity in determining the exact pressures and temperatures. However, recent studies have shown that well-ordered IrO₂(110) surfaces can be produced by epitaxial growth of IrO₂ on RuO₂(110) and TiO₂(110) surfaces. Calculations based on the Wulff construction indicate that the most stable Ir oxide surface is the (110), so the interfacial energies should give a significant contribution to result in the observed multiphase oxide surface. The calculations also indicate that the surface energies, compared to other oxides, scale as: TiO₂ < RuO₂ < SnO₂ < IrO₂, making the IrO₂ surfaces in general less stable.

Finally, upon reduction using 5 mbar CO partial pressure, we concluded that the IrO₂ bulk oxide islands reduce into metallic and epitaxial (111)- and (221)-oriented islands along with a roughening of the Ir(100) surface. This tends to recover over time, although based on our observations, the surface cannot return to a pristine state. While maintaining minor refacetting. The formation of metallic islands in the IrO₂ upon reduction confirms recent observations and form an interesting mixed metal-oxide catalyst. Interestingly, such mixed catalysts have also been observed previously on PdO(101) and thus could be a general phenomenon under oxidation conditions or for reducible oxide catalysts. In particular, the oxidation—reduction cycle is interesting, which could perhaps result in a multifunctional catalyst with a dynamic ability to store and release oxygen as the gas composition is changing.

■ CONCLUSION

In this study we investigated the stepwise oxidation and the subsequent reduction of an Ir(100) model catalyst at 775 K and a total pressure of 500 mbar by means of HESXRD. We have identified three distinct bulk oxide orientations, IrO₂(100) and IrO₂(101) the feature in each case two different domains, as well as IrO₂(110)R27°, which presents four different domains. We also observed pressure dependencies of the IrO₂ orientations, with a predominance of IrO₂(101) across pressures. We found that already at a partial oxygen pressure of 2.5 mbar oxide formation may set in consisting of the coexistence of a c(2 × 2)-O superstructure (likely along with a corrugation of the Ir(100) surface) and the onset of IrO₂(110) bulk oxide island formation. At an O₂ partial pressure of 5 and 10 mbar the surface features the coexistence of IrO₂(110), IrO₂(101), and IrO₂(100), where the IrO₂(101) orientation clearly predominates. Under reducing conditions of 5 mbar partial CO pressure, we concluded that the IrO₂ islands of different orientations reduce almost simultaneously into metallic epitaxial Ir(111) and Ir(221) islands. Our study shows that HESXRD allowed to unravel the complexity of the surface structural changes of an Ir(100) model catalyst and its oxides, a sample system of utmost interest for low-temperature CH₄ activation.
Further information about the polar figures, the detailed timeline of the experiment, the temporal evolution of the IrO$_2$ bulk oxides, additional 2D HESXR images of rotational scans and timescans measured during both oxidation cycles, an explanation for the diffraction signals of tilted IrO$_2$ bulk oxide islands, HESXR in-plane maps and line-scans deduced from rotational scans of the oxidized Ir(100) surface used for the deduction of the epitaxial relationship of the IrO$_2$ bulk oxides with respect to the substrate surface (PDF).

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