In Situ Monitoring of Nanoparticle Formation during Iridium-Catalysed Oxygen Evolution by Real-Time Small Angle X-Ray Scattering

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Real-time Small Angle X-Ray Scattering (SAXS) has been used to investigate the homogeneity of a series of molecular iridium complexes during water oxidation catalysis in aqueous NaIO₄ solution through a continuous flow cell. The results obtained for the unstable [Cp*Ir(OH)₃]⁺ precursor forming amorphous IrO₂ nanoparticles (NPs) in-situ validate and complement previous Dynamic Light Scattering (DLS) studies by providing enhanced sensitivity for small particle sizes and increased temporal resolution under realistic reaction conditions. Correlating particle formation profiles with O₂ evolution traces allowed homogeneous catalysis to be clearly distinguished from heterogeneous catalysis. A series of seven pyridine–alkoxide Cp*Ir complexes are shown to be fully homogeneous by SAXS, validating previous studies and confirming their catalysis to be molecular in nature throughout the reaction.

Introduction

Chemical energy conversion by means of water splitting is widely recognised as a key strategy for mitigating the problem of intermittency of many renewable energy sources.[1-5] Efficient water oxidation catalysts (WOCs) are required for minimising energy losses during electrolysis,[24–28] and improving their stability under the demanding operational conditions is a persistent challenge.[6,10–12] The fate of molecular precursors is particularly difficult to elucidate,[13–15] even as the seemingly simple question of whether the catalysis is homogeneous or heterogeneous in nature can be hard to address with certainty.[16–20] This is particularly true for precursors of metals which may form conductive oxide clusters, nanoparticles or thin films that are also active in water oxidation, such as ruthenium and iridium.[21–23] Efficient iridium precursors have to strike a particularly fine balance between a sacrificial placeholder ligand to be degraded during activation (e.g. Cp*)[14,24–28] and a robust chelate ligand that remains bound to the metal to modulate its activity and prevent degradation into IrO₂ nanoparticles (e.g. pyridine–alkoxides).[29,30]

Previous investigations into the speciation of half-sandwich Cp*Ir(III) precatalysts under oxygen evolution conditions in aqueous solution (Figure 1) have been carried out using dynamic light scattering (DLS) as a probe for in-situ nanoparticle formation.[29] IrCl₃, [Cp*IrCl₂] and [(Cp*Ir)(OH)]⁺→[(Cp*Ir(OH)₃)]⁺ (IrA, Figure 2) have all been found to form large, amorphous IrO₂ particles of several hundred nm in size after a lag phase of 2–20 minutes, and their growth profile was strongly influenced by [Ir] concentration, oxidant loading, solvent and pH. The initial formation of very small (primary) NPs remained beyond the detection range and sensitivity of DLS, however. Other Cp*Ir precursors bearing various chelate ligands (including Ir1, Figure 2) showed no signs of IrO₂ formation during and after O₂ evolution, suggesting these systems to be fully homogeneous within the accuracy of the DLS analysis.[29]

Investigating ligand effects in the privileged family of pyridine–alkoxide ligands for Ir-based WOCs, we recently reported a series of derivatives of Ir1 with high activity for both

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water and C–H oxidation (Ir2–7, Figure 2).\(^\text{[18,43]}\). While we have previously distinguished precursor activation from catalysis, and observed pronounced ligand effects on turnover across the different substitution patterns, the homogeneity of complexes Ir2–7 under O\(_2\) evolution conditions has not been investigated yet.

Non-crystalline diffraction based on Small Angle X-ray Scattering (SAXS) has seen extensive use in the characterisation of heterogeneous catalysts in low ordered environments.\(^\text{[33–36]}\) Due to X-rays being scattered by electron density differences, SAXS is especially sensitive for aggregates of heavy elements (such as iridium) in light matrices (e.g. aqueous solution) down to 0.1 nm length scales.\(^\text{[33]}\) Additionally, it is not restricted to diffusional conditions as light scattering techniques are, meaning that more realistic reaction conditions with active mixing may be investigated.\(^\text{[35]}\) SAXS has been used to determine the speciation of metal-oxo clusters\(^\text{[37]}\) and the growth of metal nanoparticles in solution, both using static measurements\(^\text{[38]}\) and in flow.\(^\text{[39,40]}\) Polyoxometalate (POMs) based catalysts, which are often plagued from similar homogeneity ambiguities as molecular precursors,\(^\text{[18,43]}\) have been investigated for in-situ agglomeration using SAXS.\(^\text{[44]}\) However, the use of X-ray scattering to monitor the homogeneity of molecular catalysis has only recently seen development.\(^\text{[45]}\) Here we apply SAXS to investigate the speciation of iridium precursor complexes IrA-7 under typical water oxidation reaction conditions from aqueous NaIO\(_4\) at room temperature. Independent O\(_2\) evolution experiments serve to correlate the formation of IrO\(_2\) NPs with the reaction progress to elucidate the potential involvement of any IrO\(_2\) NPs in water oxidation catalysis.

Results and Discussion

Using a quartz capillary flow cell connected to a magnetically stirred batch reactor via a peristaltic pump, background SAXS data could be collected on a flow of freshly prepared oxidant solution before a concentrated catalyst solution was injected into the reactor via a remote-controlled syringe pump to start the reaction (see experimental section and supporting information for details). We chose to investigate literature conditions of 2.5–5 mM [Ir] with 250–500 mM [NaIO\(_4\)] in neat water and native pH at room temperature to allow direct comparison with previous reports, particularly Crabtree and Elimelech’s DLS investigation.\(^\text{[29]}\)

The background-subtracted scattering profiles collected during O\(_2\) evolution catalysis with complex IrA showed the reaction solution to be a genuinely homogeneous phase with no scattering objects present over the first 22 minutes of the reaction (Figure 3). Thereafter some minor scattering features appeared in the SAXS profiles, which slowly grew in intensity over the following 6–8 minutes before noticeable X-ray scattering was detected from 30 minutes after initiating the catalysis. Figure 4a depicts the total scattering intensity across all q values from the data shown in Figure 3 over time, in comparison with previously published DLS data collected under identical conditions (Figure 4b).\(^\text{[29]}\) As it can be seen, the major NP formation event around t = 30 min was detected by both techniques. However, while no meaningful results could be derived from the correlation function of the DLS data prior to the onset of large NP formation (blue shaded region in Figure 4b), SAXS was able to detect significant scattering intensity during the nucleation phase (blue shaded region in Figure 4a; for details see data fitting below).

As nanoparticle growth kinetics are strongly affected by concentration,\(^\text{[46]}\) we also investigated a reaction at double...
precursor and oxidant loading (Figure 5). In this case the time it took for NPs to develop from IrA was almost halved ($t = 14.5$ min), and overall scattering intensity increased by close to an order of magnitude due to a larger number of NPs being formed. The Porod oscillations in $q$ observed at early stages of NP formation ($t \sim 16$ min) are fingerprints of narrow initial size distributions that quickly grew out into polydispersity over time (as shown by smooth $q$ curves from $t > 18$ mins, Figure 5).

Data Fitting

In order to derive particle size distributions, the SAXS data were fitted using a spherical body model. Checking scattering profiles from different stages of the reaction showed a good fit between the experimental data and the model used (Figure 6). While there was some slight deviation in the pre-nucleation stage (due to very low signal intensities), during NP nucleation and growth the spherical fit matched the experimental data well with $\chi^2$ values of $< 2$ (for details see the supporting information).

The size plot shown in Figure 7a illustrates the monodisperse onset of small NP formation from $t = 20–28$ mins at [IrA] = 2.5 mM. At [IrA] = 5 mM, where NP formation occurred almost twice as rapidly, the lifetime of the small, monodisperse NPs formed initially was lower, and larger, polydisperse aggregates formed more quickly from them (Figure 7b).

A close-up of the first few minutes of NP formation clearly showed the emergence of primary particles $< 4$ nm from a homogeneous solution, which then transformed into larger agglomerates that initially were fairly monodisperse (Figure 8a). This narrow initial size distribution was lost within 2–3 minutes after their formation, broadening out to a distribution of larger particle sizes up to 200 nm. While the latter observation is similar to previous DLS results (Figure 4b), the additional detection of small NPs prior to the appearance of larger...
agglomerates by SAXS is valuable information for their mechanism of formation, and allows deeper insight into the origin of the catalysis.

The rapid increase in size of the small NPs fitted a mono-exponential growth function (Figure S5) consistent with a classical La Mer mechanism \cite{46,48,49} consisting of an initial nucleation burst followed by growth within a constant particle volume (Figure 8b).\cite{50–52} Total scattering intensities derived from DLS decreased over time as sedimentation set in,\cite{29} an effect which was not apparent in the actively mixed flow system investigated by SAXS. Particle growth must be aggregative rather than proceeding via Ostwald ripening, as indicated by the continued presence of small NPs throughout the duration of the experiment (note two particle size distributions at $t=...$)

Figure 5. SAXS data for IrA (5 mM) at room temperature injected into 500 mM NaIO$_4$ (100 equiv) in H$_2$O at $t=0$ (30 s intervals, data baseline subtracted).

Figure 6. SAXS data (points with error bars) versus spherical model fit (solid lines) during pre-nucleation (3, 5, 11 minutes), nucleation (14.5, 15.5, 16.5 min) and post-nucleation (25, 45, 60 min) stages of IrO$_x$ NP formation from IrA at room temperature (5 mM $\pm$ 500 mM NaIO$_4$).

Figure 7. Relative volume fractions of IrO$_x$ nanoparticles formed from IrA (a: 2.5 mM, b: 5 mM) with 100 equiv. NaIO$_4$ in H$_2$O at room temperature over time.
The pronounced dependence of time, rate and amount of NP formation on [Ir] concentration (see Figures 3 and 5) is consistent with super-saturation of the solution being the driver for the initial nucleation burst.50

Cp*Ir(pyalk) Precursor Complexes

Having established the utility of SAXS as a highly sensitive technique to detect small IrOx NPs during O2 evolution catalysis with molecular precursors, the more active pyalk-ligated Cp*Ir complexes Ir1–7 were investigated for homogeneity. The setup and conditions were identical as for the IrA complex, with the reaction initiated by addition of the precatalyst to the flowing oxidant solution (100 equiv. NaIO4). The baseline-subtracted data for Ir1 depicted in Figure 9a shows a distinct lack of any scattering objects over the entire duration of the experiment. Similar to previous DLS results, no features characteristic of NPs could be found in any of the 120 measurements collected over 1 hour, even with the much more sensitive SAXS measurement. The detection limit under the conditions applied was estimated to be around 1.4 ppm of IrOx clusters of 4 nm size in an aqueous solution containing 483 ppm of homogeneously dissolved [Ir]. Thus, these results unambiguously confirm the previous conclusion of Ir1 forming a molecular catalyst species that is stable towards IrOx formation under reaction conditions.29,53

Moving to other substitution patterns not previously investigated for homogeneity, complexes Ir2–7 also showed no scattering features under identical conditions. In-situ SAXS showed a consistent lack of any signs for nanoparticle formation over the course of the reaction in all cases (Figures 9a and S3). As both DLS and SAXS measurements have consistently shown that any small IrOx NPs formed would eventually

Figure 8. (a) IrOx NP formation from IrA (5 mM) with 100 equiv. NaIO4 in H2O at room temperature. (b) Volume fraction of initial NPs with r < 4 nm (green) and their relative volume fraction in solution (blue) over the course of the reaction.

Figure 9. (a) SAXS data for Ir1 (2.5 mM) with 250 mM NaIO4 (30 s intervals, data baseline subtracted). (b) Relative scatter volumes for Ir1–Ir7 (all 2.5 mM Ir, injected into 250 mM NaIO4 in H2O at room temperature) obtained from data fitting. Occasional scattering events are due to bubble formation or undissolved catalyst precursor.
agglomerate, we can thus confidently conclude that the entire class of Ir1–7 are truly molecular oxidation catalysts.[32]

Correlation with Catalytic O₂ Evolution

It was previously reported that the amorphous IrOₓ NPs recovered at the end of the reaction with labile WOC precursors were also active in O₂ evolution catalysis themselves.[17,29,54] In order to further elucidate the role of any NPs in catalysis starting from molecular precursors, we correlated the in-situ SAXS profiles with O₂ evolution traces. Figure 10a shows the activities of precatalysts Ir1–7 under SAXS conditions as derived from headspace manometry, which mirror their relative initial rates previously measured electrochemically in solution.[32] Overlaying O₂ evolution activity with X-ray scattering intensity for Ir1 as an example (Figure 10b) clearly shows that the solution remained homogeneous during and after the reaction, and that the catalyst must be a stable molecular entity.

By contrasting SAXS intensity with O₂ evolution activity for the unstable complex IrA (Figure 11), we could show that NP formation only set in after the reaction had come to completion (> 22 minutes). Thus, any catalytic activity observed must have originated from molecular species even in case of the unstable aqua complex. IrOₓ formation appeared to be a post-catalytic transformation, and any NPs observed at the end of the reaction were thus not the active species generating O₂.[17,54]

In order to compare the homogeneous and heterogeneous forms of IrA in catalysis, additional portions of NaIO₄ were added to the solution after completion of IrOₓ NP formation after 1 hour (Figure 12a). As it can be seen from the profiles of O₂ evolution and the corresponding catalytic rates summarised in Table 1, the IrOₓ NPs formed after the first cycle were about four times more active than the initial homogeneous catalyst form of IrA. As the large NPs > 200 nm possess low surface fractions of Ir atoms, we tentatively ascribe the majority of the activity observed to arise from the remainder of small NPs < 4 nm present in the mixture (see Figures 7 and 8b), although at present we cannot exclude the possibility of NP redissolution or leaching of molecular species as seen in other catalytic systems.[55] The pyalk-ligated catalyst Ir1 on the other hand showed over 10 times higher activity than IrA with higher TONs, consistent rates and no NP formation over at least three cycles (Figure 12b), confirming the notion of a well-defined and stable molecular catalyst entity supported by the pyridine–alkoxide ligand.

Table 1. Observed turnover numbers (TON) and turnover frequencies (TOF) of O₂ evolution upon sequential additions of oxidant to IrA and Ir1 in H₂O at room temperature (2.5 mM [Ir] + 100 equiv. NaIO₄ each time).

| Catalyst | Oxidant addition | TON[a] | TOF[b] [min⁻¹] | NPs |
|----------|------------------|--------|----------------|-----|
| IrA      | 1                | 24     | 1.2            | x   |
|          | 2                | 28     | 5.0            | ✓   |
|          | 3                | 28     | 4.7            | ✓   |
| Ir1      | 1                | 38     | 17.4           | x   |
|          | 2                | 39     | 14.3           | x   |
|          | 3                | 38     | 17.7           | x   |

[a] n(O₂)/n(Ir); [b] TON/time (initial slope 0.6–1.5 min).
Using a simple recirculating flow setup with remote-controlled sample addition, we have shown the utility of real-time SAXS as a non-invasive tool for investigating nanoparticle formation during operationally homogeneous catalysis with molecular precursors in solution. With synchrotron X-ray sources and CCD detectors highly sensitive measurements could be acquired at good temporal resolution of < 1 min. SAXS profiles contain a wealth of particle shape and dispersity information extractable by quantitative modelling, and additional X-ray absorption and diffraction patterns may be collected to obtain further insight into the composition and morphology of the NPs if required. In case of the eight molecular WOC precursors Ir1-7 investigated during catalytic O₂ evolution from aqueous NaIO₄ solutions, SAXS has been able to detect small IrO₂ clusters of < 4 nm formed from [Cp*Ir(OH)₂]SO₄ that had escaped previous DLS analyses. Correlation with O₂ evolution profiles showed NP formation to be a post-catalytic transformation, forming a heterogeneous catalyst mixture that is more active than the initial molecular species in the absence of an organic ligand. On the other hand, a family of seven pyridine–alkoxide ligated Cp*Ir complexes have been shown to be > 99.7% homogeneous throughout the reaction by SAXS. These solutions give higher activities and may be reactivated with identical rates by repeat addition of fresh oxidant, firmly establishing the molecular origin of the catalysis and lending weight to previous mechanistic proposals based on homogeneously dissolved bis-μ-oxo iridium dimers and tetrameramers protected from polymerisation to IrO₂ by the pyridine–alkoxide ligands.[31] We hope that these findings will help to assist the development of improved catalysts for water splitting and other applications where the important question of catalyst homogeneity has remained difficult to address.[16–20]

Experimental Section

General. All chemicals were purchased from major commercial suppliers and used as received. Ultrapure DI water (18.2 mΩ) was supplied from an Elga deionisation unit (Diamond Light Source, Harwell). Syntheses were performed under argon using standard Schlenk techniques. [(η⁵-pentamethylcyclopentadienyl)Ir(OH)₂]SO₄ was prepared following an adapted literature procedure,[35] iridium complexes Ir1-7 were prepared according to literature procedures,[31] and all analytical data were in agreement with reported values.

Analysis – Experimental set-up. In a typical experiment, the desired amount of oxidant (535 mg, 2.5 mmol or 1070 mg, 5.0 mmol) was dissolved in 9 mL water in air. The resulting clear solution was passed through a 0.2 μm PTFE syringe filter into a 30 mL glass vial magnetically stirred at 400 RPM and flowed through a 1.35 mm I.D. quartz capillary at a rate of 26 mL min⁻¹ via a peristaltic pump with silicone tubing. 1 mL of aqueous catalyst solution (containing 0.025 mmol Ir) were added via a remote-controlled syringe pump to start the reaction after having collected a background measurement. SAXS data were continuously collected in 30 s intervals for 1 hour at room temperature. In between each catalytic run the flow setup was flushed with at least 50 mL DI water. The scattering pattern of the empty capillary checked after runs 5, 10 and 14 showed no deposition of any nanoparticles.

Analysis – Small Angle X-ray Scattering (SAXS). Time-resolved SAXS measurements were carried out at the I22 beamline at the Diamond Light Source (Harwell, UK) using a beam energy of 12.4 keV. The sample to detector distance was calibrated to 9.763 m using a silicon nitride diffraction grating with a period of 100 nm (Silson, UK). Data were collected on a Pilatus3 2M photon counting hybrid pixel detector (Dectris AG, Switzerland). The usable q-range for this experiment geometry was 0.0015 < q < 0.167 Å⁻¹, giving access to scattering from objects in the size range of 37–4180 Å. Data were placed onto an absolute intensity scale by comparing scattering from a piece of calibrated glassy carbon (NIST SRM3600) collected during the experiment, with the reference dataset.[31] Data were corrected and reduced using the DAWN package[58,59] and standard pipelines developed at Diamond.[60]

Models for SAXS. The Scattering Length Density (SLD) contrasts were calculated using the assumption of IrO₂(OH)₂ particles with a density of 11.66 g cm⁻³ to give a SLD contrast of 6.96 eÅ⁻² calculated for a 250 mM solution of NaIO₂ as the matrix (composition of 0.25 Na, 0.25 I, 55.52 O, and 111.05 H) with an overall density of 1.053 g cm⁻³. A total of 120 SAXS patterns were measured per kinetic run and fitted with a spherical model using...
Sampling and Analysis of the Oxidation Products

The oxidation products were analyzed using a high-performance liquid chromatography (HPLC) system equipped with a diode-array detector. The samples were eluted using a linear gradient of acetonitrile and water containing 0.1% formic acid. The chromatograms were integrated to quantify the concentrations of the individual products.

**Results and Discussion**

The results of the HPLC analysis showed that the oxidized iron complex underwent a selective oxidation reaction, predominantly forming a single product identified as a hydroxylated derivative. The yield of the product was quantified to be 85%, with no significant formation of by-products.

**Conclusions**

The selective oxidation of iron complexes using the established conditions demonstrates the potential for this method in the synthesis of iron-containing compounds. Further studies are recommended to explore the applicability of this method to other metal complexes and to investigate the mechanism of the oxidation process.

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**Conflict of Interest**

There are no conflicts of interest.

**Keywords**

HPLC, iron complexes, oxidative coupling, by-products, product yield.
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