



Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal: <https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a “*preliminary report*”),
- even for experiments whose scientific area is different from the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.

- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: Understanding the origin of CO oxidation activity at single Ru(II) site: a combined Ru L ₃ and Cl K edge RIXS study	Experiment number: CH-6683
Beamline: ID26	Date of experiment: from: 06-06-2023 to: 11-06-2023	Date of report: 08-09-2023
Shifts: 18	Local contact(s): Dr. Pieter Glatzel	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Yifei Ren¹ Daniel Wan¹ Guanghan Zhu¹ Ryan Wang¹ <ol style="list-style-type: none"> Laboratory University College London (UCL) Material and Catalysis Lab LB18, Roberts building, Torrington place GB - WC1E7JE LONDON 		

Report:

1. Abstract

Ru(II) compounds are widely used in catalysis, photocatalysis and medical applications. They usually obtained in reductive environment as molecular O₂ can oxidize Ru(II) to Ru(III) and Ru(IV). Here we have designed an air-stable surface $-\text{[bipy-Ru(II)(CO)}_2\text{Cl}_2\text{]}$ site that is obtained by reduction of $-\text{[bipy-Ru(III)Cl}_4\text{]}$ - with simultaneous ligand exchange from Cl⁻ to CO. The $-\text{[bipy-Ru(II)(CO)}_2\text{Cl}_2\text{]}$ site enables oxidation of CO with a turnover frequency of $0.73 \times 10^{-2} \text{ s}^{-1}$ at 462 K, while the Ru(III) site is completely inert.

2. Experiment details

Fresh sample, sample after step 1, 2 and 3 treatment are first being measured ex-situ, together with RuCl₃, RuO₂ and NaCl as standards. Furthermore, fresh sample is measured in-situ. 1% CO and 1% O₂ was introduced into the chamber, then the sample was heat up from room temperature to 200 °C. Ru L₃ edge and Cl K edge XAFS were measured during heat up. Then after cooling down in the same gas condition, 1% H₂ was further introduced into the chamber, the sample was then het up to 300 °C, Ru L₃ edge and Cl K edge XAFS were measured during heat up. After cooling down to room tempertuare, the gas condition changes to 1% CO and 1% O₂ again then heat up to 300 °C. Ru L₃ edge and Cl K edge XAFS were measured during heat up.

3. Results

The HERDF-XANES measurement use the Ru 3d to 2p emission as the fluorescence detection, which significantly increases the energy resolution. In this study we have three spin states: $t_{2g}^4e_g^0$, $t_{2g}^5e_g^0$, and $t_{2g}^6e_g^0$. The RuO_2 has a double features that are corresponded to $2p_{3/2} \rightarrow 4dt_{2g}$ and $2p_{3/2} \rightarrow 4de_g$ excitation with a $t_{2g}^4e_g^0$ configuration (Fig. 1a blue). RuCl_3 has a $t_{2g}^5e_g^0$ configuration. Due to the distortion in the lattice, the further split of the e_g level leads to a broad feature that is difficult to fit (Fig. 1a, red). This is in good agreement with the literatue report.¹ Our fresh sample $-\text{[Ru(bipy)Cl}_4\text{]H}$ has the $t_{2g}^5e_g^0$ without any distrotrion from the crystal. Therefore, the $2p_{3/2} \rightarrow 4dt_{2g}$ and $2p_{3/2} \rightarrow 4de_g$ excitations are clearly visible (Fig. 1a black). With only one hole at t_{2g}^5 , the $2p_{3/2} \rightarrow 4dt_{2g}$ has much lower probability than $2p_{3/2} \rightarrow 4de_g$. The first activation step should form $-\text{[Ru(bipy)COCl}_3\text{]}$ species, which keeps Ru at 3+ with Cl^- replaced by CO. The Ru 2p to CO π^* transition is clearly visible at 2842 eV (Fig. 1b green) is higher than that of $2p_{3/2} \rightarrow 4de_g$ transition, which helps to confirm the relative orbital energy in Fig. 2. Interestingly, the $2p_{3/2} \rightarrow 4dt_{2g}$ has also decreased significantly, suggesting completely occupied t_{2g} orbitals. This may due to the strong σ bonding from the CO 2σ to $4d_{xy}$ orbital.

Moving to step 2, in which H_2 is used to reduce Ru^{3+} to Ru^{2+} . The Ru 2p to CO π^* transition decreases in intensity even with 2 CO ligands coordinate with the Ru^{2+} (Fig. 2c).

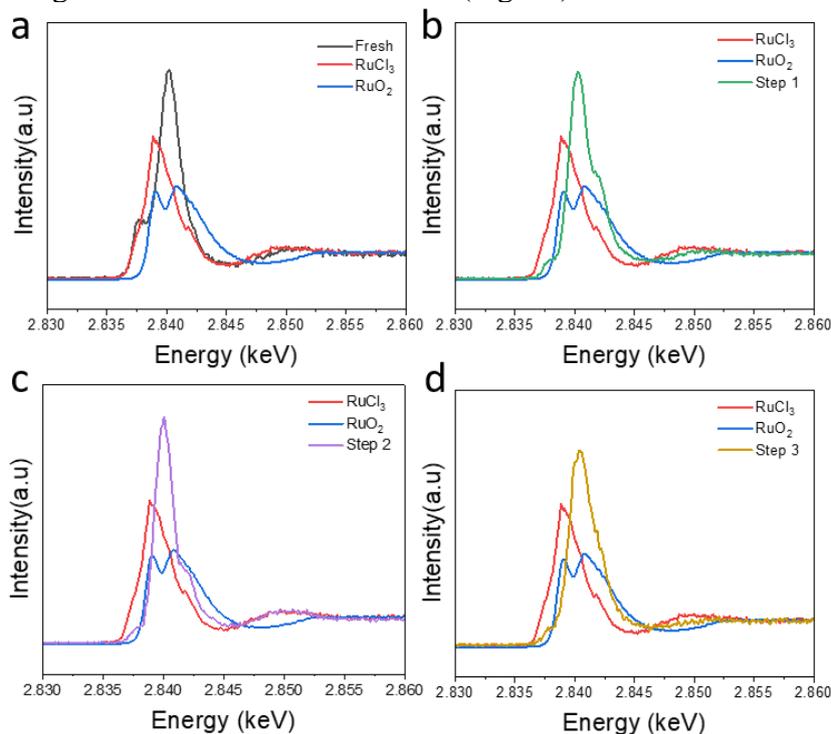


Figure 1. *Ex situ* Ru L₃ edge of **a.** Fresh sample **b.** sample after step 1 **c.** sample after step 2 **d.** sample after step 3 with RuCl_3 and RuO_2 as reference.

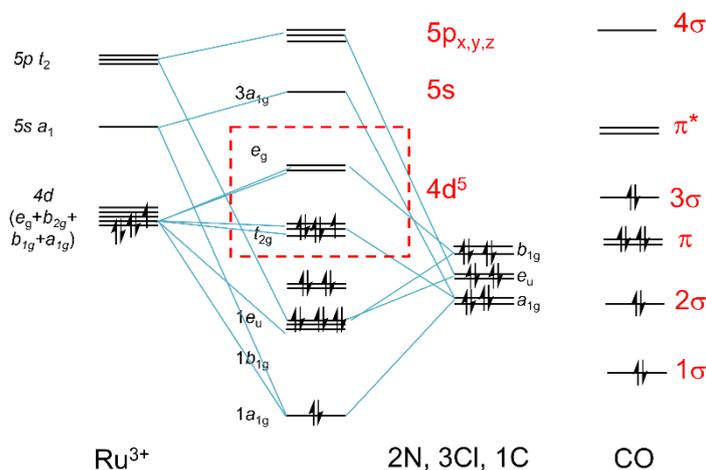


Figure 2. The molecular orbital diagram of $-\text{[Ru(bipy)COCl}_3\text{]}$.

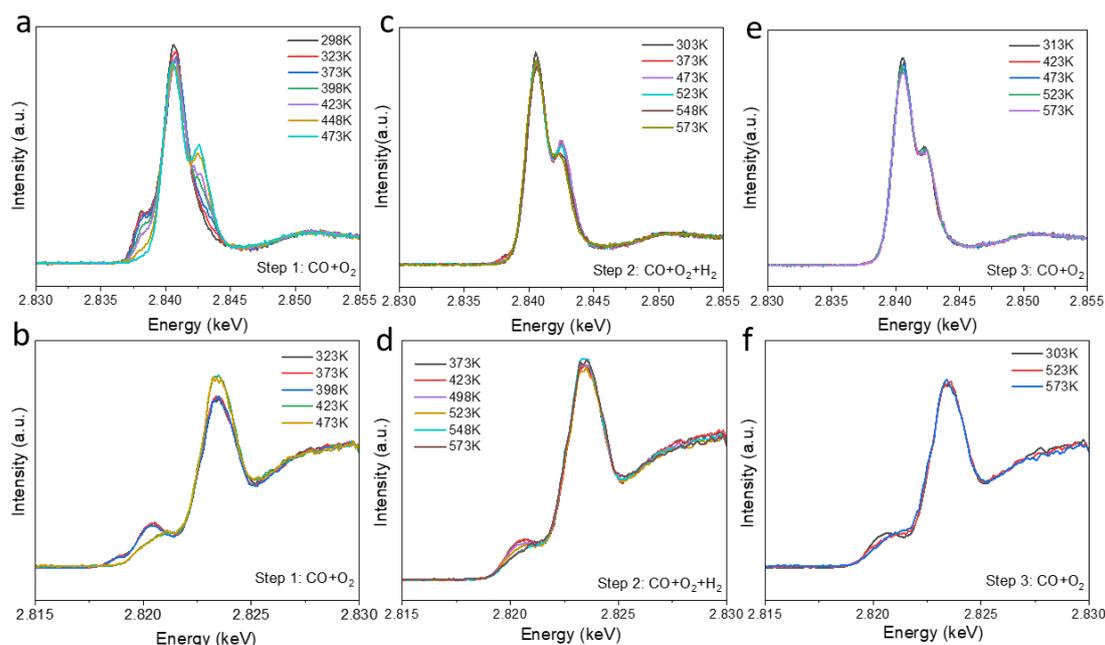


Figure 3. *In situ* Ru L₃ and Cl K edge of during **a.b.** step 1 treatment, **c.d.** step 2 treatment, **e.f.** step 3 treatment.

Moreover, the process showed in Figure 1 was further investigate *via in-situ* measurement together with Cl K edge measurement. Fig. 3a shows the reduction of Ru starts from 373K and at 473K, the feature at 2837.7 eV disappears completely with the formation Ru 2p to CO π^* transition at 448 K, suggesting a simultaneous Ru³⁺ reduction and CO insertion. This is beyond our current knowledge as we thought step 1 is a simply ligand exchange reaction. The corresponded Cl K edge spectra showed a decrease in the Cl 1s to Ru 4d t_{2g} transition, further confirms that CO will reduce the Ru³⁺ in the step 1. In step 2, H₂ is introduced with another CO coordination to Ru. This leads to a slight blue shift of the Ru 2p to CO π^* transition with decreased intensity. It is not clear why the probability of such transition has been decreased slightly (Fig. 3b). The Cl K edge spectra show mainly the Cl 1s to Ru e_g transition. Step 3 is the real CO oxidation environment, so both Ru and Cl do not change during the reaction.

4. Discussion, conclusions and future work

The reduction of Ru(III) and the formation of *cis*(CO)-*trans*(Cl)-[Ru(bipy)(CO)₂Cl₂] sites has been confirmed by both Ru L₃ edge and Cl K edge measurement. In the step 1, the ligand exchange and Ru³⁺ reduction take place at 448 K. In step 2, the further ligand exchange with the formation of HCl happens at 548 K. However, it is not clear why the Ru 2p to CO π^* transition has a blue shift when the second CO molecule is coordinated with Ru²⁺. It is also not clear what is the oxidative product for the step 1 as we do not see any CO₂ formation. Both require further investigation. We still have the Ru core to core RIXS data that can be analyzed and reported in the future. Further explanation of the spectra requires careful calculations, which is sought in collaborations.

5. Reference

1. PHYSICAL REVIEW B 96, 161107(R) (2017)