Real Time Determination of the Electronic Structure of Unstable Reaction Intermediates during Au₂O₃ Reduction

Jakub Szlachetko,*†‡∇ Jacinto Sá,†§,$ Jean-Claude Dousse,# Joanna Hoszowska,# Daniel Luis Abreu Fernandes,‖ Hongqing Shi,¶ and Catherine Stampfl‖¶

†Paul Scherrer Institut, Villigen, Switzerland
‡Institute of Physics, Jan Kochanowski University, Kielce, Poland
§LSU Group, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
‖Department for Chemical and Bioengineering, ETH Zurich, Zurich, Switzerland
#Department of Physics, University of Fribourg, Fribourg, Switzerland
∥Department of Chemistry, University of Aveiro, Aveiro, Portugal
¶School of Physics, The University of Sydney, Sydney, Australia

ABSTRACT: Chemical reactions are always associated with electronic structure changes of the involved chemical species. Determining the electronic configuration of an atom allows probing its chemical state and gives understanding of the reaction pathways. However, often the reactions are too complex and too fast to be measured at in situ conditions due to slow and/or insensitive experimental techniques. A short-lived Au₂O compound has been detected for the first time under in situ conditions during the temperature-programmed reduction of Au₂O₃. A time-resolved resonant inelastic X-ray scattering experiment (RIXS) allowed the determination of changes in the Au electronic structure, enabling a better understanding of the reaction mechanism of Au(III) reduction. On the basis of time-resolved RIXS data analysis combined with genetic algorithm methodology, we determined the electronic structure of the metastable Au₂O intermediate species. The data analysis showed a notably larger value for the lattice constant of the intermediate Au as compared to the theoretical predictions. With support of DFT calculations, we found that such a structure may indeed be formed and that the expanded lattice constant is due to the termination of Au₂O on the Au₂O₃ structure.

Chemical reactions are driven by the electronic structure of the valence shell of the catalytic active metal. The availability of valence orbitals to form chemical bonds, and thus take part in the chemical reaction, depends on their electron occupancy and energy.¹⁻² Therefore, the characterization of the electronic structure of catalysts before, during, and after a reaction is vital for the fundamental understanding of materials performance and stability.

Resonant inelastic X-ray scattering (RIXS) spectroscopy offers great potential to study the electronic structure of the catalytic site. RIXS is a photon-in, photon-out scattering technique where the incoming photon excites the atom to an intermediate state, which decays to its final state by the emission of a photon. RIXS combines X-ray absorption, which reflects the unoccupied density of states (DOS) and X-ray emission processes, which characterizes the occupied DOS and thus allows for a detailed investigation of the local electronic structure of the metal of interest. Furthermore, thanks to the penetrating properties of hard X-rays, RIXS can be performed in situ, thus providing information about occupied and unoccupied electronic states of catalysts under working conditions.³⁻⁷ Moreover, the RIXS has been recognized as a most powerful technique, as compared to commonly applied X-ray absorption spectroscopy (XAS) techniques, to study the electronic structure of matter.⁸⁻¹¹

To obtain meaningful information, RIXS spectroscopy requires high-energy resolution for both the incoming and outgoing X-rays. To this point, RIXS spectroscopy has been restricted to the investigation of steady-state systems because of the relatively long acquisition times imposed by the necessity of scanning the incoming and outgoing X-ray energies with high energy resolution during the experiment.⁹⁻¹¹

Herein, we report on the changes occurring in the electronic structure of Au during the temperature-programmed reduction of Au₂O₃. The electronic structure was monitored by time-resolved RIXS spectroscopy using a von Hamos type crystal
Because of the dispersive-type detection of the emitted X-rays, only the energy of the incoming X-rays is scanned; thus, the RIXS planes can be recorded at sub-minute time resolution. The recorded electronic structure changes reveal the existence of a short-lived metastable Au(I) oxide in the temperature-programmed reduction of Au$_2$O$_3$, whose electronic and geometric properties could be retrieved from the time-resolved RIXS data set with the help of a genetic algorithm.

Figure 1a shows the schematics of the RIXS process around the L$_3$ absorption edge of Au(III). By tuning the incoming X-ray energy around the L$_3$ edge (2p$_{3/2}$ electrons), the density of the unoccupied 5d states can be probed with high sensitivity thanks to the strong 2p$_{3/2} \rightarrow$ 5d dipolar excitation. Within 0.11 fs, the 2p$_{3/2}$ core hole decays then via the 3d$^5$5d$^6$s$^0$ → 2p$_{3/2}$ electronic transition; this is accompanied by the emission of an X-ray photon. Therefore, by monitoring the incoming and outgoing X-ray energies/intensities, detailed information about the electronic structure of Au$_{10}$ can be retrieved. In the present experiment, Au$_2$O$_3$ powder was loaded into a quartz capillary reactor connected to a H$_2$ inlet. The sample was heated from 20 up to 300 °C with a ramp of 5 °C per minute. The electronic structure changes were recorded at sub-minute time resolution. The recorded electronic structure changes reveal the existence of a short-lived metastable Au(I) oxide in the temperature-programmed reduction of Au$_2$O$_3$, whose electronic and geometric properties could be retrieved from the time-resolved RIXS data set with the help of a genetic algorithm.

Figure 2a shows the schematics of the RIXS process around the L$_3$ absorption edge of Au(III). By tuning the incoming X-ray energy around the L$_3$ edge (2p$_{3/2}$ electrons), the density of the unoccupied 5d states can be probed with high sensitivity thanks to the strong 2p$_{3/2} \rightarrow$ 5d dipolar excitation. Within 0.11 fs, the 2p$_{3/2}$ core hole decays then via the 3d$^5$5d$^6$s$^0$ → 2p$_{3/2}$ electronic transition; this is accompanied by the emission of an X-ray photon. Therefore, by monitoring the incoming and outgoing X-ray energies/intensities, detailed information about the electronic structure of Au$_{10}$ can be retrieved. In the present experiment, Au$_2$O$_3$ powder was loaded into a quartz capillary reactor connected to a H$_2$ inlet. The sample was heated from 20 up to 300 °C with a ramp of 5 °C per minute. The electronic structure changes were recorded at sub-minute time resolution. The recorded electronic structure changes reveal the existence of a short-lived metastable Au(I) oxide in the temperature-programmed reduction of Au$_2$O$_3$, whose electronic and geometric properties could be retrieved from the time-resolved RIXS data set with the help of a genetic algorithm.
The outcome of the experimental data, we applied the genetic algorithm procedure to recover the concentration changes of Au(III) and Au(0) during the temperature-programmed reduction experiment, the representative RIXS planes of Figure 2 were used as references to fit the 70 time-resolved RIXS spectra. The least-squares fitting procedure and analysis of fit residuals revealed that at intermediate temperatures of 140–200 °C, the experimental data could not be reproduced using only those two references. This result suggested the existence of a third Au phase (see the Supporting Information (SI) for details). In order to extract the electronic structure of this third component from the experimental data, we applied the genetic algorithm procedure (see the SI for details). The outcome of the computation is presented in Figure 3. As shown, the RIXS plane of the intermediate Au consists of a 5d resonance with a maximum located at an excitation energy of 11919.5 eV. This resonance is weaker in intensity than the one observed in the case of Au2O3 but stronger than that in the case of Au(0). Furthermore, weak structures were detected at higher excitation energies, at around 11934 and 11948 eV, respectively. The detection of a third component in the time-resolved RIXS data suggests that the Au2O3 reduction occurs in two steps, possibly with the formation of Au(I) according to the following reaction path:

\[
\begin{align*}
\text{Au}_2\text{O}_3 + 2\text{H}_2 & \rightarrow \text{Au}_2\text{O} + 2\text{H}_2\text{O} \\
\text{Au}_2\text{O} + \text{H}_2 & \rightarrow \text{Au}^0 + \text{H}_2\text{O}
\end{align*}
\]

Despite being a credible and possible reduction mechanism, evidence for Au2O formation is scarce. The main reason is that Au(I) oxide is an endothermic system and metastable with respect to O2 and metallic Au. As predicted by theoretical calculations, the bulk Au2O phase forms into the cuprite structure with a fcc lattice. We used this theoretical structure estimation to calculate the electronic DOS of Au using the FEFF9.0 code and the Kramers–Heisenberg formulas for the RIXS process. The calculated RIXS plane is presented in Figure 3b. As shown, good agreement was achieved with the experimental data because all three RIXS features could be well-reproduced. The agreement is particularly good around the edge. The discrepancy in the post-edge region relates to the fact that the features in this region are naturally broad due to multiple scattering processes; however, the features are detectable within the measurement error. In Figure 3c, we plot the high energy resolution X-ray absorption spectrum extracted from the peak intensity variation of the Lα transition. The spectrum is compared to the theoretical one, together with the DOS of Au in the Au2O structure. Similar to Au(III) and Au(0), the Au(I) oxide white line is composed of unoccupied d orbitals, while the s, p, and f states do not contribute significantly to the spectrum. The two structures at higher excitation energies relate to the multielectron scattering effects, the contribution from other orbitals being negligible.

We should note here that in order to match the theoretical calculations with the experimental RIXS data, the lattice constant of the Au(I) oxide in the fcc form had to be expanded from 4.8 to 5.3 Å. For the temperature at which the Au(I) oxide was detected (140–200 °C), this relatively big mismatch cannot be explained by thermal expansion. The reduction of the Au2O3 particle follows a shell-to-core mechanism, where first the outside of the particle is reduced. The process then continues constantly from the outer shell to the inside of the particle. In this case, the Au(I) oxide may be formed in the sample as a thin layer located between the Au2O3 and Au(0) structures. For this reason, we investigated how the Au2O phase would terminate on the Au2O3 structure.

In order to validate the Au2O termination hypothesis, we performed surface formation energy calculations using the DFT total energy Vienna ab initio simulation package (VASP). To investigate the relative stability of a thin layer of Au2O(001) on Au2O3(001) (see Figure 4a and b) as compared to the structure with a fcc lattice. We used this theoretical structure estimation to calculate the electronic DOS of Au using the FEFF9.0 code and the Kramers–Heisenberg formulas for the RIXS process. The calculated RIXS plane is presented in Figure 3b. As shown, good agreement was achieved with the experimental data because all three RIXS features could be well-reproduced. The agreement is particularly good around the edge. The discrepancy in the post-edge region relates to the fact that the features in this region are naturally broad due to multiple scattering processes; however, the features are detectable within the measurement error. In Figure 3c, we plot the high energy resolution X-ray absorption spectrum extracted from the peak intensity variation of the Lα transition. The spectrum is compared to the theoretical one, together with the DOS of Au in the Au2O structure. Similar to Au(III) and Au(0), the Au(I) oxide white line is composed of unoccupied d orbitals, while the s, p, and f states do not contribute significantly to the spectrum. The two structures at higher excitation energies relate to the multielectron scattering effects, the contribution from other orbitals being negligible.

We should note here that in order to match the theoretical calculations with the experimental RIXS data, the lattice constant of the Au(I) oxide in the fcc form had to be expanded from 4.8 to 5.3 Å. For the temperature at which the Au(I) oxide was detected (140–200 °C), this relatively big mismatch cannot be explained by thermal expansion. The reduction of the Au2O3 particle follows a shell-to-core mechanism, where first the outside of the particle is reduced. The process then continues constantly from the outer shell to the inside of the particle. In this case, the Au(I) oxide may be formed in the sample as a thin layer located between the Au2O3 and Au(0) structures. For this reason, we investigated how the Au2O phase would terminate on the Au2O3 structure.

In order to validate the Au2O termination hypothesis, we performed surface formation energy calculations using the DFT total energy Vienna ab initio simulation package (VASP). To investigate the relative stability of a thin layer of Au2O(001) on Au2O3(001) (see Figure 4a and b) as compared to the
unreconstructed Au₂O₃(001) surface (Figure 4c), we used the approach of ab initio atomistic thermodynamics. We employed the projector augmented wave method (PAW) and the generalized gradient approximation (GGA) for the exchange−correlation functional (for details, see the SI). The simulations showed that at zero temperature and O-rich conditions (delta O-chem pot = 0), the two-layer Au₂O₃ structure has the lowest formation energy, but for increasing temperature, the one-layer AuO becomes lower in energy (delta O-chem pot ≅−0.1 eV). This is consistent with the fact that the time-resolved RIXS experiment detects the presence of Au₂O. What should be also noticed is that the lattice constant in the b direction of Au₂O₃ is around 10.68 Å. This is approximately twice as much as the value of 5.3 Å found for the AuO lattice constant (10.68 Å/2 = 5.34 Å). Further, the lattice constant of Au₂O in the a direction is around 13.06 Å, and this value multiplied by 2 (26.12 Å) is about five times bigger than 5.3 Å (26.12 Å/5 = 5.23 Å). In summary, this means that the surface of 10 unit cells of Au₂O(001) fits the surface of 2 (along the a axis) × 1 (along the b axis) Au₂O₃(001) unit cells. The latter is in agreement with the experimental results and confirms the detection of the Au₂O phase with an expanded lattice parameter as a termination structure of Au₂O₃.

Using the three RIXS references of Au phases, we employed least-squares fitting to the time-resolved data in order to follow the concentration of Au species as a function of temperature. The outcome of the fitting is plotted in Figure 5. The Au₂O₃ reduction starts at temperatures of around 100 °C with a smooth decrease in concentration of about 10−20% up to 180 °C. A quick decrease is detected at temperatures of 180−220 °C with simultaneous increase of the Au(0) concentration. At a temperature of 200 °C, a 50/50 ratio between Au₂O₃ and Au is detected. The intermediate AuO species are detected at temperatures of 100−200 °C and at a maximum level of concentration of about 7−8%. This low level of detected AuO, as compared to the other two species, is synonymous with the fact that, once formed, the AuO is quickly reduced to Au(0), that is, a short-lived intermediate. The observation confirms that AuO is involved in the reduction of Au₂O₃ to Au(0) as the reaction intermediate. Furthermore, because AuO is thermodynamically unstable, it decomposes to metallic Au very quickly, especially at higher temperatures.

The ability to determine the dynamic electronic structure of the chemical site under working conditions with appropriate time resolution enables the determination of short-lived structures that are often responsible for the chemical reactivity. Flavel56 said recently, “At present, the mechanisms of very few reactions are understood in detail — measurement techniques are usually too slow to monitor the intermediates formed. It is a bit like only being able to see who crosses the finishing line first in a race, and not how they got there.” The proposed approach of using time-resolved RIXS enables us to follow the race and to determine all involved species. This is particularly important for gold chemistry, where there is large controversy with respect to the active oxidation state of gold. Most of the suggested active gold states were formulated based on pre- and postreaction analysis.

**ASSOCIATED CONTENT**

Supporting Information
The Experimental details, including theoretical calculations and genetic algorithm overview.

**AUTHOR INFORMATION**

Corresponding Authors
*E-mail: jakub.szlachetko@psi.ch (J. Szlachetko).
*E-mail: stampf@physics.usyd.edu.au (C. Stampf).

Author Contributions
J. Szlachetko and J. Sá contributed equally to the manuscript.
The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

The authors would like to acknowledge the Swiss Light Source, from the Paul Scherrer Institute (Switzerland), for access to the X10DA (SuperXAS) beam line. The authors thank Prof. van Bokhoven for the fruitful discussions.

**REFERENCES**


