X-ray Induced Reduction of Rhenium Salts and Supported Oxide Catalysts

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Abstract

The analysis of Re^{7+} compounds has revealed a time-dependent photoreduction during x-ray photoelectron spectroscopy (XPS) measurements. Whilst such reduction of metal ions during XPS analysis is not uncommon, this is the first time that cases specifically for rhenium have been identified in the open literature.

Keywords

XPS, photoelectron, rhenium, reduction, oxide

Introduction

The photoreduction of organic materials during x-ray photoelectron spectroscopy (XPS) analysis is well known[1], as is the reduction of metal ions, for example, Au^{3+}, Cu^{2+} and Pd^{2+}.[2-5] However, recent analysis of supported rhenium catalysts indicate that higher valence rhenium states also undergo reduction, which hitherto has not been addressed in the open literature.

Rhenium itself, despite its rarity and consequential cost is widely used in high-performance alloys, such as those used in turbines or jet engines where corrosion resistance and low thermal deformation is required[6] and also finds application in smart materials such as shape-memory alloys[7] and organic light-emitting diode (OLED) devices.[8]

Rhenium is also used in in catalysis. Pt-Re based catalysts for example, are used for the catalytic reforming of low-octane naphtha to high-octane petrol[9], because of their excellent resilience to poisoning from sulfur and phosphorous.[10, 11] Rhenium is also used for olefin metathesis, where typically Re_2O_7 is supported on alumina[12, 13], partial oxidation[14] and dehydrogenation reactions.[15] Clearly, the diverse uses of rhenium requires an exact knowledge of the surface species present, if the chemistry is to be fully understood.

Rhenium as an oxide, typically exists in +7 through to +4 oxidation states[16] and, from the literature it is clear there is a wealth of older XPS data available on Re oxidations states, which is made up of a combination of data from Re-supported catalysts[14, 17-23] and more conventional model surface science experiments[14, 23]. These papers report binding energies that cover a wide range of values for distinct rhenium oxidation states.[24]

To address these discrepancies, Griener *et al.* investigated a range of bulk rhenium oxides as reference compounds for their synchrotron based studies of rhenium oxidation.[14] Whilst this study generated

a self-consistent set of binding energies and also indicated mixed Re states depending on the oxide and treatment conditions, no evidence of the formation of reduced states via photoreduction was noted or discussed.[14]

The purpose of this communication therefore is to introduce to the literature, the degradation of Re^{7+} states during XPS analysis which, unless accounted for, could lead to an incorrect picture of the rhenium states present in these high valence materials.

Experimental

All data were acquired on a Thermo-Fisher Scientific K-Alpha$^+$ x-ray photoelectron spectrometer, utilising monochromatic Al Kα radiation operating at a power of 72 W (6 mA x 12 kV). High resolution scans were performed at a pass energy of 40 eV, with a 0.1 eV step, whilst survey spectra were acquired at a pass energy of 150 eV and a step size of 1 eV. Charge neutralisation was achieved using a combination of low energy electrons and argon ions which gave a reproducible C(1s) binding energy of 284.8 eV for all samples.

To investigate the reduction, the Re(4f) region was collected multiple times before collection of other spectral regions and multiple samples from the same batch were analysed to ensure consistency. All samples gave nominally similar amounts of reduction that are within the errors of fitting.

Samples of 1% Re/ZnO and ammonium perrhenate, NH_4ReO_4, were analysed. The latter was supplied by Sigma Aldrich and analysed as received, whilst the 1% Re/ZnO sample was prepared by a standard wet impregnation method reported previously.[25] In a typical synthesis the NH_4ReO_4 was added to 2 ml deionised water and stirred for approximately 15 min. The ZnO support was added to the solution and stirred to form a paste. The paste was subsequently dried at 110 °C for 16 h, and calcined in static air (400 °C, 8 h, 5 °C min^{-1}). Briefly, TEM results reveal the 1% Re/ZnO sample consists of a distribution of metal oxide particles (*ca.* 10 – 30 nm) on rectangular ZnO rafts varying between *ca.* 200 – 400 nm in size.

Results and Discussion

Figure 1 shows the Re(4f) spectra taken after 2 scans of the Re region (analysis time *ca.* 1 minute) for as received ammonium perrhenate and the 1% Re/ZnO catalyst. Both give rise to an identical Re(4f$_{7/2}$) binding energy of 46.3 eV with a spin-orbit splitting 2.4 eV; the elemental composition of each sample is given in table 1.

For the most intense rhenium peaks, the Re(4f$_{7/2}$) binding energy value is almost 1 eV higher than that determined by Griener for Re^{7+} in Re_2O_7[14], but in good agreement with that reported for Re^{7+} from other studies.[18-20, 23, 26] Of importance for the purpose of this communication however is the asymmetry toward the lower binding energy of the main photoelectron peak. This intensity will be subsequently shown to be attributable to photoreduced states.

Figure 2 shows the effect of x-rays on the Re oxidation states. Here the Re(4f) region was acquired via multiplex scanning for a period of *ca.* 5 min for each acquisition, with a total sampling time of approximately 100 min. The increase in the lower binding energy peaks is clear in this time frame, and the relative percentage obtained by fitting of each Re(4f$_{7/2}$) state is shown in figure 2.

From the data presented in figure 3, a small shift (0.2 eV) in peak position during the first few analysis cycles is evident and is within experimental confidence limits. Assuming the most intense Re species is Re[7+], then the lower two oxidation states can be attributed to Re[6+] (44.7 eV) and Re[4+] (43.5 eV).[24] It is prudent to note that although these values differ from those of Greiner *et al.*[14], the energetic difference *between* oxidation states of, for example Re[7+] and Re[6+], are broadly comparable to those of Greiner (difference of *ca.* 0.3 to 0.4 eV) and strengthens these assignments. Previous studies of ammonium perrhenate revealed an initially complex mix of rhenium states prior to argon sputtering, after which a well resolved Re(4f) doublet (46.4 and 48.8 eV) was noted, together with rhenium states below *ca.*45 eV which were attributed to reduced states introduced *via* the sputtering process.[22]

For the Re/ZnO sample, a more pronounced reduction is observed over an identical timeframe, however in this instance there is a difference in the binding energies obtained by fitting . The higher energy Re(3d$_{5/2}$) peak has a binding energy of 46.3 eV and again assigned to Re[7+]. The lower two oxidation states have binding energies of 43.9 and 42.6 eV respectively (0.8 eV lower than the equivalent species in the perrhenate), but we assign these to Re[6+] and Re[4+] species.[20]
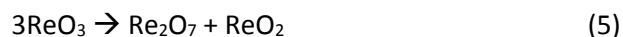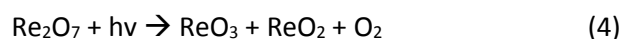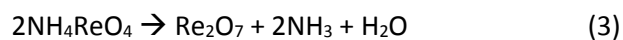
Clearly there is no difference in the Re[7+] binding energy, and therefore the question remains why the lower oxidations states differ to those of the perrhenate. Whilst this is an area for future investigation, the difference in binding energies for the Re[6+] and Re[4+] states between the two samples is tentatively attributed to of particle size/distribution and the influence of possible ligand effects. For example, the perrhenate is a pure compound with large crystallites which also contains NH_4^+, whereas the supported catalyst comprises of dispersed nanoparticulate (10 – 20 nm) rhenium oxide (Re_2O_7) species. The influence on particle size and the observed binding energy is well known [27-30] and therefore may have some influence on the difference in the binding energy of the Re[6+] state for example.

In respect of the rate of reduction, photoreduction during XPS analysis is well established [2-5] and clearly a similar phenomenon for rhenium is observed. In comparison to the perrhenate, the increased rate of reduction for the supported catalyst may be explained by the greater propensity toward photoreduction for nanoparticles because of their size and volume compared to a larger, bulk-like material. Interestingly, similar spectra to those of the reduced species were obtained by Babu and Mucalo in their work on freshly prepared rhenium colloids,[31] wherein they concluded fresh samples contained multiple rhenium oxidation states; however the dominating species remained Re[7+] and their employment of a non-monochromatic source would lead to a more rapid reduction. Therefore, it is believed the reduced states observed are due to photodegredation and as such colloidal rhenium is an area which would be beneficial to re-examine in light of the current results.

In terms of a decomposition pathway, the results always reveal 6+ and 4+ oxidation states in addition to the major Re[7+] species, which is unsurprising given that the stable binary rhenium oxides are Re_2O_7, ReO_3 and ReO_2.[32] Re_2O_7 itself sublimes at relatively low temperatures for a metal oxide (*ca.*150 °C)[14], whilst ReO_3 is reported to disproportionate to Re_2O_7 and ReO_2,[32] so a propensity for reduction exists. It is easy therefore to envisage the following to pathways for the oxide, which would account for a rapid increase in the Re[4+] state and a relatively stable Re[6+] species.

$$Re_2O_7 + h\nu \rightarrow ReO_3 + ReO_2 + O_2 \qquad\qquad (1)$$

$$3ReO_3 \rightarrow Re_2O_7 + ReO_2 \qquad\qquad (2)$$
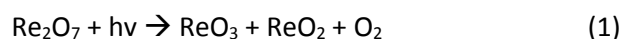
A similar decomposition pathway would be expected for the perhenate, although ammonia would presumably be liberated akin to the following:

$$2NH_4ReO_4 \rightarrow Re_2O_7 + 2NH_3 + H_2O \qquad (3)$$

$$Re_2O_7 + hv \rightarrow ReO_3 + ReO_2 + O_2 \qquad (4)$$

$$3ReO_3 \rightarrow Re_2O_7 + ReO_2 \qquad (5)$$

Conclusions

We have shown that bulk-like and supported rhenium in the 7+ oxidation state undergoes photoreduction akin to that observed for Au^{3+}, Pd^{2+} and Cu^{2+} species; with nanoparticulate materials undergoing a more rapid reduction.

To the best of the authors' knowledge, this is the first time the photoreduction of rhenium has been reported in the open literature, and serves to illustrate that care should be taken in the methodology used for acquiring rhenium XPS data and the subsequent analysis of the data. Additionally from this study, it is evident that it would be beneficial to the surface analysis community for a systematic reinvestigation on a number of rhenium compounds.

Acknowledgements

References

[1]   G. Beamson, D. Briggs, *High Resolution XPS of Organic Polymers: The Scienta ESCA300 Database*, Wiley, **1992**.
[2]   V. Di Castro, G. Piredda, *Chemical Physics Letters* **1985**, *114*, 109.
[3]   Y. Y. Fong, B. R. Visser, J. R. Gascooke, B. C. Cowie, L. Thomsen, G. F. Metha, M. A. Buntine, H. H. Harris, *Langmuir : the ACS journal of surfaces and colloids* **2011**, *27*, 8099.
[4]   S. Poulston, P. M. Parlett, P. Stone, M. Bowker, *Surface and Interface Analysis* **1996**, *24*, 811.
[5]   S. Suzer, *Applied Spectroscopy* **2000**, *54*, 1716.
[6]   F. Lang, T. Narita, *Intermetallics* **2007**, *15*, 599.
[7]   H.-J. Kang, S.-K. Wu, L.-M. Wu, *Intermetallics* **2010**, *18*, 123.
[8]   Y. Jia, L. Duan, D. Zhang, J. Qiao, G. Dong, L. Wang, Y. Qiu, *The Journal of Physical Chemistry C* **2013**, *117*, 13763.
[9]   R. Burch, *Platinum Metal Reviews* **1978**, *22*, 57.
[10]   B. M. Pavlikhin, L. I. Vlasova, M. Y. Levinter, *Petroleum Chemistry U.S.S.R.* **1981**, *21*, 82.
[11]   C. R. Hammond, *"The Elements" in Handbook of Chemistry and Physics (81st ed.).* , CRC Press, **2004**.
[12]   J. C. Mol, *Catalysis Today* **1999**, *51*, 289.
[13]   A. K. Coverdale, P. F. Dearing, A. Ellison, *Journal of the Chemical Society, Chemical Communications* **1983**, 567.
[14]   M. T. Greiner, T. C. R. Rocha, B. Johnson, A. Klyushin, A. Knop-Gericke, R. Schlögl, *Zeitschrift für Physikalische Chemie* **2014**, *228*.
[15]   C. Betizeau, G. Leclercq, R. Maurel, C. Bolivar, H. Charcosset, R. Frety, L. Tournayan, *Journal of Catalysis* **1976**, *45*, 179.
[16]   F. A. Cotton, G. Wilkinson, *Advanced inorganic chemistry*, John Wiley & Sons, Incorporated, **1988**.
[17]   E. Brockawik, J. Haber, L. Ungier, *Journal of Physics and Chemistry of Solids* **1981**, *42*, 203.
[18]   A. Cimino, D. Gazzoli, M. Inversi, M. Valigi, *Surface and Interface Analysis* **1986**, *9*, 245.
[19]   A. Cimino, D. Gazzoli, M. Inversi, M. Valigi, *Surface and Interface Analysis* **1987**, *10*, 194.
[20]   A. S. Fung, P. A. Tooley, M. J. Kelley, D. C. Koningsberger, B. C. Gates, *The Journal of Physical Chemistry* **1991**, *95*, 225.
[21]   M. Garland, A. Baiker, A. Wokaun, *Industrial & Engineering Chemistry Research* **1991**, *30*, 440.
[22]   M. Komiyama, Y. Ogino, Y. Akai, M. Goto, *J Chem Soc Farad T 2* **1983**, *79*, 1719.
[23]   W. T. Tysoe, F. Zaera, G. A. Somorjai, *Surface Science* **1988**, *200*, 1.
[24]   NIST X-ray Photoelectron Spectroscopy Database, Version 4.1, National Institute of Standards and Technology, Gaithersburg, **2012** (http://srdata.nist.gov/xps/).
[25]   G. M. King, S. Iqbal, P. J. Miedziak, G. L. Brett, S. A. Kondrat, B. R. Yeo, X. Liu, J. K. Edwards, D. J. Morgan, D. K. Knight, G. J. Hutchings, *ChemCatChem* **2015**, *7*, 2122.
[26]   X. Yide, W. Xinguang, S. Yingzhen, Z. Yihua, G. Xiexian, *Journal of Molecular Catalysis* **1986**, *36*, 79.
[27]   J. Radnik, C. Mohr, P. Claus, *Physical Chemistry Chemical Physics* **2003**, *5*, 172.
[28]   M. Sankar, Q. He, M. Morad, J. Pritchard, S. J. Freakley, J. K. Edwards, S. H. Taylor, D. J. Morgan, A. F. Carley, D. W. Knight, C. J. Kiely, G. J. Hutchings, *ACS Nano* **2012**, *6*, 6600.
[29]   J. G. Tao, J. S. Pan, C. H. A. Huan, Z. Zhang, J. W. Chai, S. J. Wang, *Surface Science* **2008**, *602*, 2769.
[30]   P. Rodriguez, D. Plana, D. J. Fermin, M. T. M. Koper, *Journal of Catalysis* **2014**, *311*, 182.
[31]   K. M. Babu, M. R. Mucalo, *Journal of Materials Science Letters* **2003**, *22*, 1755.
[32]   G. Rouschias, *Chemical Reviews* **1974**, *74*, 531.

Table 1. XPS derived molar composition (atomic %) for both rhenium samples

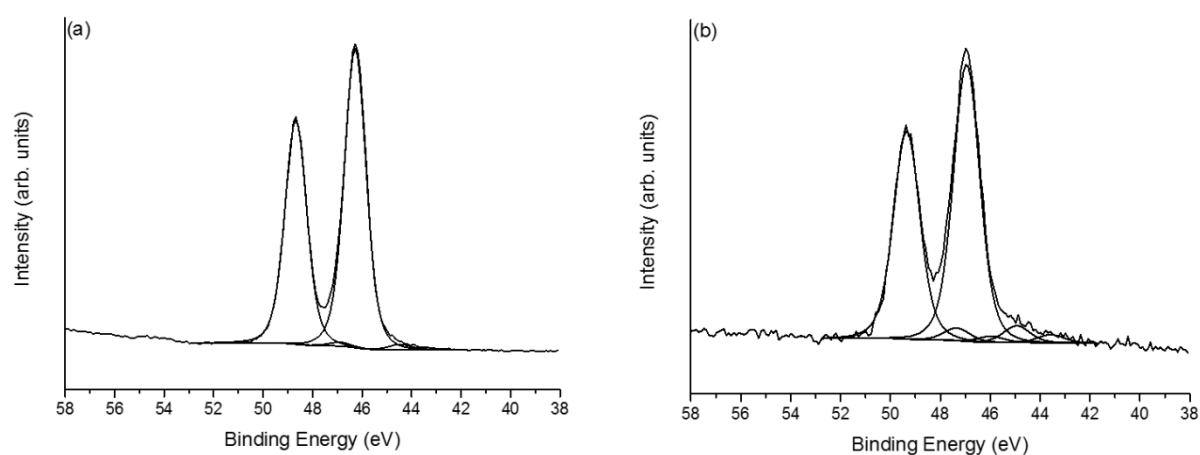| Sample	Atomic %					
	Re	O	N	Zn	Na	C
NH$_4$ReO$_4$	16.59	59.53	16.97	0.00	3.37	3.54
1% Re/ZnO	1.52	47.15	0.00	41.80	0.00	9.53

Figures

Figure 1. Initial Re(4f) spectra for (a) ammonium perrhenate, NH_4ReO_4 and (b) 1% Re/ZnO. Both spectra are taken after 2 scans of the Re(4f) region totalling ca. 1 minute
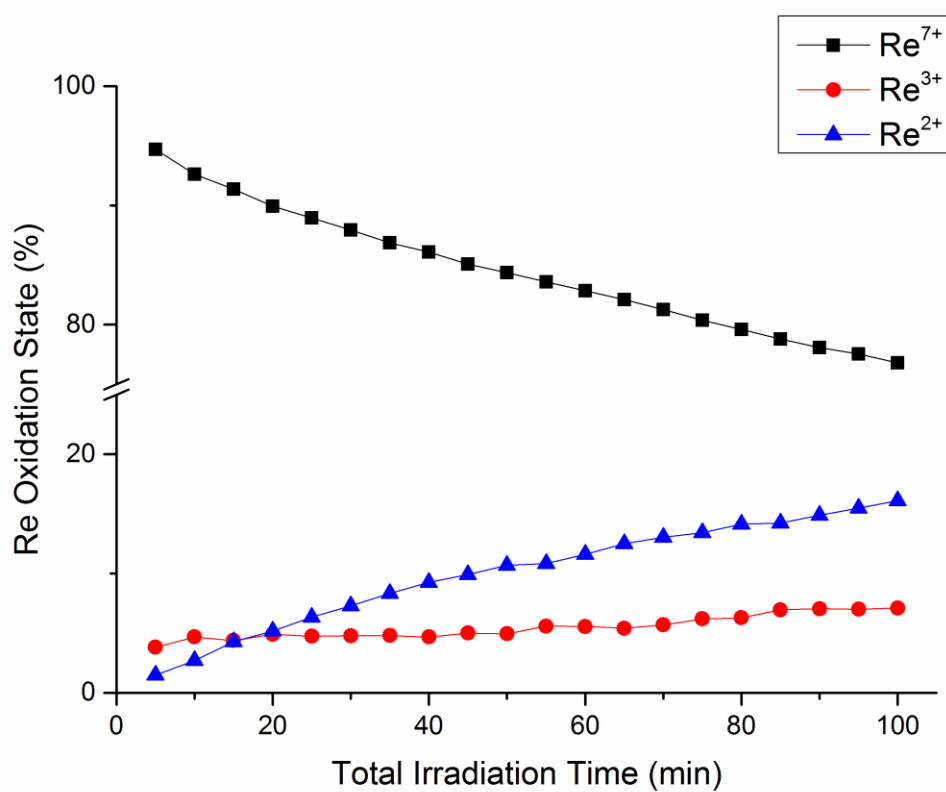

Figure 2. Plot of change in oxidation states during XPS analysis of ammonium perrhenate, NH_4ReO_4.
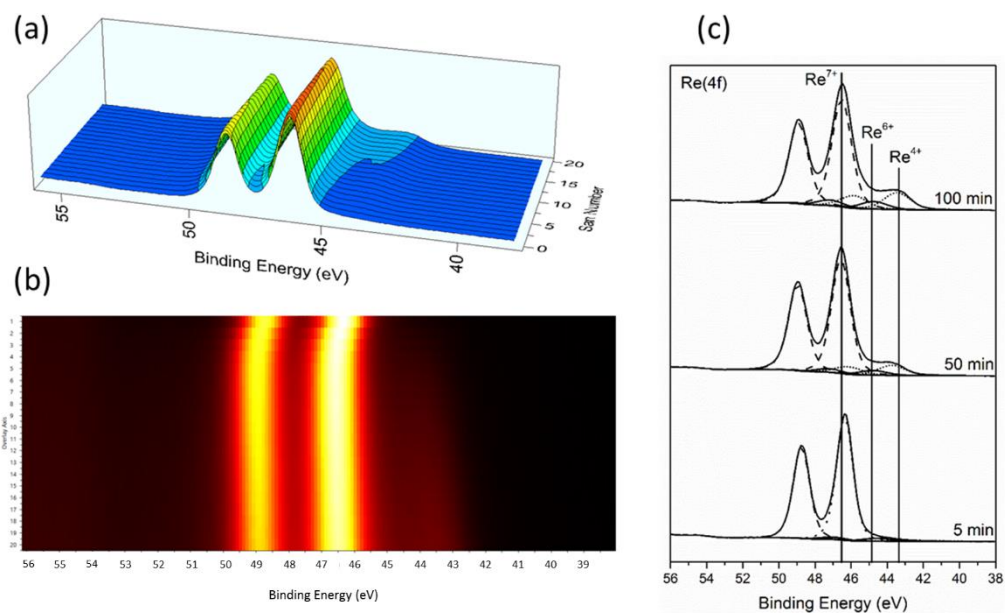
Figure 3. Re(4f) core-level spectra plotted as (a) coloured contour-waterfall, (b) photoelectron intensity map and (c) stacked plots to illustrate the effect of x-ray irradiation of ammonium perrehnate over a period of ca. 100 min. Note that (a) and (b) are plotted for all 100 minutes, whilst (c) shows only the 5, 50 and 100 minute plots for clarity
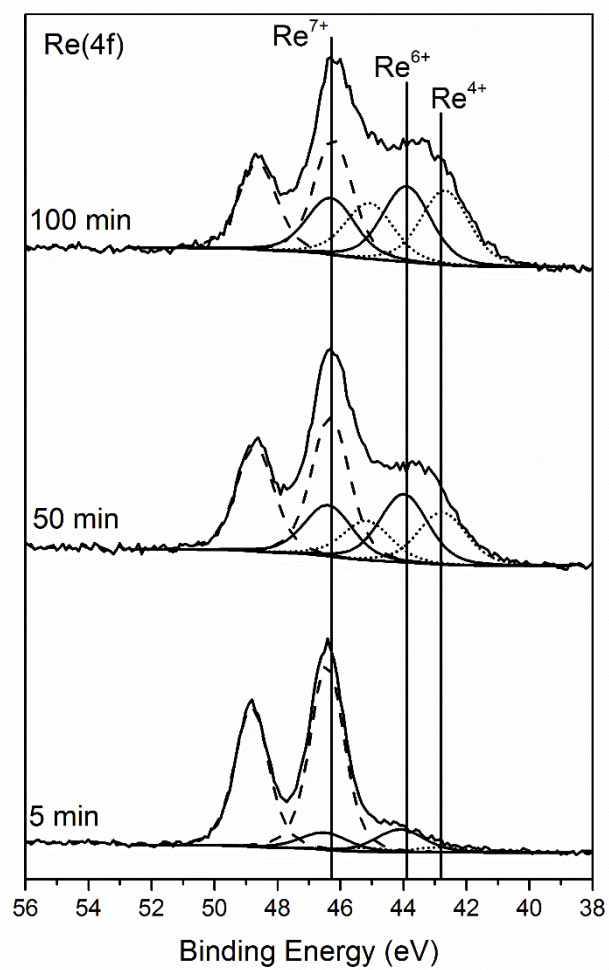
Figure 4. Re(4f) core-level spectra for the photoreduction of a 1% Re/ZnO catalytic sample after 5, 50 and 100 minutes of irradiation