X-ray photoelectron spectroscopy as a probe of the interaction between rhodium acetate and ionic liquids

Shuang Men [a,b,c,*,1], Jing Jiang [d,1]

[a] School of Material Science and Engineering, Shenyang Ligong University, Shenyang 110159, PR China
[b] School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK
[c] Institute of Applied Ecology, Chinese Academy of Sciences, Shenyang 110016, PR China
[d] School of Mechanical Engineering and Automation, Northeastern University, Shenyang 110004, PR China

ARTICLE INFO

ABSTRACT

X-ray photoelectron spectroscopy (XPS) is used as a probe of the interaction between rhodium acetate ($[Rh_2(OAc)_4]$) and ionic liquids. Due to the impact of the anion of ionic liquids on the electronic environment of the rhodium centre, the measured Rh 3d binding energies of $[Rh_2(OAc)_4]$ dissolved in a series of ionic liquids were found to decrease along with the increasing of the basicity of anions. The reduction of Rh(II) to Rh(0) in 1-octyl-3methylimidazolium acetate ($[C_8C_1Im][OAc]$) under UHV condition was monitored by XPS. The intensity of the new formed metallic Rh(0) peak was found increased along with time. The surface enrichment of the new formed Rh(0) species in the system was also concluded.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Over the past decade, ionic liquids have attracted an expanding interest from not only academic but also industrial sources [1,2]. The widespread investigation of ionic liquids now provides with opportunities to understand in more depth, many processes, *i.e.* organic synthesis and catalysis.

Ionic liquids have very low vapour pressures which enable themselves to be placed into an Ultra High Vacuum (UHV) chamber and analysed by XPS without any specific modification of the experimental set-up at room temperature [3,4]. XPS has now become a widely used technique for the analysis of pure ionic liquids and ionic liquid-based systems. Since 2005, XPS investigations have been mainly focused on the elemental composition, surface enrichment and the change of the electronic environment of a certain component present in ionic liquids [3,5–8]. It has been probed by XPS that the basicity of the anion has significant impact on the electronic environment of the cation component for a range of ionic liquids, such as imidazolium- [9], pyrrolidinium- [10], and pyridinium-based ionic liquids [11]. Furthermore, XPS data can be correlated to NMR data [12] and Kamlet-Taft parameters [9,13] to allow further understanding of properties of ionic liquids. Apart

from that, XPS has also been used to identify the subtle change in electronic environment of the metal centre within halometallate anions [13–15] and phosphineimidazolylidene metal containing cations [16]. However, the inner sphere changes, *i.e.* the interaction between ionic liquids and a catalyst which only acts as the solute in the solution, is until now not properly investigated.

Switching from traditional organic solvents to ionic liquids can usually give rise to the enhancement of the solubility and stability of catalysts. However, as has been reported, some catalysts which were tested to be stable, have been observed to be reduced to form metallic species (0) in ionic liquid reaction systems, *i.e.* palladium catalysts [17–21] and rhodium catalysts [22]. XPS has the ability to distinguish between different oxidation states of metal catalysts in ionic liquid-based solutions [23,24].
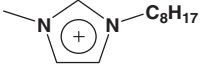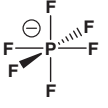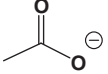
In this study, we choose $[Rh_2(OAc)_4]$, which is a widely used catalyst in C-H insertion, cyclopropanation and allylic oxidation reactions [25,26] as an innocent solute in ionic liquids. We investigate four $[Rh_2(OAc)_4]$ containing ionic liquid-based solutions employing $[C_8C_1Im]^+$ as the cation with commonly used anions, *i.e.* hexaflurophosphate ($[PF_6]^-$), bromide (Br^-), chloride (Cl^-) and $[OAc]^-$. The measured binding energies of Rh 3d were found to decrease along with the increasing of the anion basisity of ionic liquids. Moreover, the reduction of Rh(II) to Rh(0) was observed in the case of $[OAc]^-$. The intensity of the new formed metallic Rh(0) peak was found increased along with time. The surface enrichment of the new formed Rh(0) species was also concluded based upon the calculation of concentrations of $[Rh_2(OAc)_4]$ containing ionic liquid-based solutions from XP spectra.

* Corresponding author at: School of Material Science and Engineering, Shenyang Ligong University, Shenyang 110159, PR China.
E-mail address: menshuang@hotmail.com (S. Men).
[1] These authors are contributed equally to this work.

Table 1
Structures of the polyatomic ions investigated in this study.

Abbreviation	Structure	Name
$[C_8C_1Im]^+$		1-octyl-3-methylimidazolium
$[PF_6]^-$		hexafluorophosphate
Br^-		bromide
Cl^-		chloride
$[OAc]^-$		acetate

2. Experimental

2.1. Materials

All chemicals were obtained from Sigma–Aldrich or Alfa Aesar and were used as received except for 1-methylimidazole, which was distilled over calcium hydride prior to use. All ionic liquids investigated in this study were prepared in Nottingham Ionic Liquids Group using established synthetic protocols, $[C_8C_1Im][PF_6]$ [27], $[C_8C_1Im]Br$ [27], $[C_8C_1Im]Cl$ [27], and $[C_8C_1Im][OAc]$ [28]. The structures of the individual cations and anions investigated in this study are shown in Table 1.

All ionic liquids were dried *in vacuo* ($p \leq 10^{-3}$ mbar) before being fully characterised by ^1H NMR spectroscopy, ^{13}C NMR spectroscopy, ESI-MS and Karl Fischer titration. When ion exchange was one of the synthetic steps, ion chromatographic analysis (both anion and cation) showed that residual ion concentrations (Cl^-, Li^+, Na^+, Ag^+) were all below accepted threshold concentrations, *i.e.*, <10 ppm. In all cases, no residual signal of either halide, or metal ions were observed during XPS analysis, *i.e.*, the concentration was below the limit of detection. Full data, including full XPS data sets with peak deconstruction models, for all of the materials studied in this work appears in the Electronic Supplementary Information (ESI).

2.2. XPS data collection

All XP spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al Kα source ($h\nu = 1486.6$ eV), hybrid (magnetic/electrostatic) optics, hemispherical analyser and a multi-channel plate and delay line detector (DLD) with a X-ray incident angle of 30° and a collection angle, θ, of 0° (both relative to the surface normal). X-ray gun power was set to 100 W. All spectra were recorded using an entrance aperture of 300 μm × 700 μm with a pass energy of 80 eV for survey spectra and 20 eV for high-resolution spectra. The instrument sensitivity was 7.5×10^5 counts s^{-1} when measuring the Ag 3d$_{5/2}$ photoemission peak for a clean Ag sample recorded at a pass energy of 20 eV and 450 W emission power. Ag 3d$_{5/2}$ full width half maximum (FWHM) was 0.55 eV for the same instrument settings. Binding energy calibration was made using Au 4f$_{7/2}$ (83.96 eV), Ag 3d$_{5/2}$ (368.21 eV) and Cu 2p$_{3/2}$ (932.62 eV). The absolute error in the acquisition of binding energies is ±0.1 eV, as quoted by the instruments manufacturer (Kratos); consequently, any binding energies within 0.2 eV can be considered the same, within the experimental error. Charge neutralisation methods were not required (or employed) in the measurement of these data. Sample stubs were earthed *via* the instrument stage using a standard BNC connector.

Samples were prepared by placing a small drop ($\approx$20 mg) of the ionic liquid into a depression on a stainless steel sample stub (designed for powders) or on a standard stainless steel multi-sample bar (both Kratos designs). The ionic liquid samples were presented as thin films (approx. thickness 0.5–1 mm), thereby avoiding experimental complications associated with variable sample height. Initial pumping to high vacuum pressure was carried out in a preparation chamber immediately after thin film preparation to avoid significant absorption of volatile impurities. Pumping of ionic liquids was carried out with care as the high viscosities associated with these samples meant that significant bubbling due to removal of volatile impurities was observed. The pumping down process was consequently carried out slowly to avoid contamination of the UHV chamber by bumping/splashing of the ionic liquid samples. The preparation chamber pressure achieved was $\approx$10^{-7} mbar. Pumping-times varied (1–3 h total) depending upon the volume, volatile impurity content and viscosity of the sample, *i.e.*, viscous ionic liquids were found to require longer pumping times. The samples were then transferred to the main analytical vacuum chamber. The pressure in the main chamber remained $\leq 1 \times 10^{-8}$ mbar during all XPS measurements, suggesting that all volatile impurities, such as water, are removed, leading to high purity samples [29].

2.3. Information depth of XPS

The information depth (ID) of XPS experiments may be defined as the depth, within the sample, from which 95% of the measured signal will originate. ID is assumed to vary mainly with cos θ, where θ is the electron emission angle relative to the surface normal. Values of λ are typically in the range of 1–3 nm [30]. If we assume that the inelastic mean free path (λ) of photoelectrons in organic compounds is of the order of $\sim$3 nm, at the kinetic energies employed here we can estimate ID in this geometry, when $\theta = 0°$, ID = 7–9 nm. Consequently these data may be considered as representative of the bulk composition and do not reflect any local enhancements of concentration at the near surface region.

2.4. XPS data analysis

For data interpretation, a linear spline background subtraction was used. Relative Sensitivity Factors (RSF) were taken from the Kratos Library and were used to determine atomic percentages [31]. Peaks were fitted using GL(30) lineshapes; a combination of a Gaussian (70%) and Lorentzian (30%) [30]. This lineshape has been used consistently in the fitting of XP spectra, and has been found to match experimental lineshapes in ionic liquid systems. The FWHM of each component was initially constrained to $0.8 \leq$ FWHM ≤ 1.5 eV. XP spectra for all ionic liquid solutions were charge corrected by setting the measured binding energy of the aliphatic C 1s component ($C_{aliphatic}$ 1s) to 285.0 eV. This procedure has been shown to be robust for all samples when alkyl substituents on charge carriers are large (*i.e.*, when $n \geq 8$) [9–11]. The presence of additional carbon in $[OAc]^-$ must be added to the existing fit model; a fitting model has been developed for charge referencing samples where the anion is $[OAc]^-$ [16,32].

2.5. Sample preparation

In this study, Rh-containing ionic liquid-based solutions were prepared by adding $[Rh_2(OAc)_4]$ into ionic liquids. Since the $[Rh_2(OAc)_4]$ shows limited and slow solubility in ionic liquids,