



X-ray photoelectron spectroscopy as a probe of rhodium-ligand interaction in ionic liquids



Shuang Men^{a,b,*}, Kevin R.J. Lovelock^c, Peter Licence^{b,**}

^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 Department of Chemistry, Imperial College London, London SW7 2AZ, UK

ARTICLE INFO

Article history:

Received 31 October 2015

In final form 9 December 2015

Available online 17 December 2015

ABSTRACT

We use X-ray photoelectron spectroscopy (XPS) to identify the interaction between the rhodium atom and phosphine ligands in six 1-octyl-3-methylimidazolium-based ionic liquids ([C₈C₁Im][X]). The formation of a mono-phosphine rhodium complex based upon addition of triphenylphosphine (PPh₃) is confirmed by XPS in all ionic liquids studied herein. Due to the electron donation effect of the ligand, the rhodium atom becomes more negatively charged and thus exhibits a lower measured binding energy. The influence of the anion basicity on the formation of different types of rhodium complexes is also investigated. By introducing a biphosphine ligand, a chelated diphosphine rhodium complex is formed in ionic liquids with more basic anions and verified by both XPS and Infrared Spectroscopy (IR). The measured Rh 3d binding energies are correlated to the reaction selectivity of a hydroformylation reaction which inspires a method to design a metal catalyst to control the chemical reaction towards desired products in the future.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Homogeneous catalysis is a large field of activity in the area of ionic liquids and has attracted lots of interests over the past decade [1–4]. Since ionic liquids exhibit a wide range of fascinating properties, *i.e.* low volatility and excellent solvating ability, they have shown huge potential for the replacement of the traditional organic solvents [2,5]. As has been reported previously, many ionic liquids can dissolve organometallic compounds, allowing them to act as suitable solvents for transition metal based catalysis.

In many cases, they have been found to be better solvents when compared to traditional organic solvents, as well as water [1]. Ionic liquids have been successfully applied to many homogeneous catalytic reactions such as hydrogenation [6], hydroformylation [3], oxidation [3], oligomerization [3] as well as coupling reactions, *i.e.* Heck reaction [7,8] and Suzuki reaction [8,9]. Using ionic liquids as reaction solvents can usually give rise to a different chemical activity of the system [10–17] and thus an acceleration

[8,9] or better selectivity towards the desired products [18,19], which renders them more valuable. An excellent example is the rhodium catalysed hydroformylation reaction. Rhodium based catalysts have been successfully applied to hydroformylation reactions in a biphasic ionic liquid/scCO₂ systems where the catalyst was firstly dissolved in ionic liquid phase and the product was extracted by scCO₂ [20–22]. In the case of reactions catalysed by (Acetylacetonato)dicarbonylrhodium(I) ([Rh(acac)(CO)₂]), a potential problem is that the catalyst can be also extracted out of the ionic liquid phase. To overcome this problem, phosphine ligands were always added into the system to enhance the solubility of the catalyst in ionic liquid phase. This procedure aimed to avoid the leaching of the rhodium catalyst from the ionic liquid phase primarily. Unexpectedly, the reaction selectivity was somehow controlled; different phosphine ligands show different reaction selectivity towards the desired linear product.

Due to the low volatility of ionic liquids, XPS has been applied to characterise the elemental composition and subtle binding energy shifts of samples since 2005, when the Licence group measured the reduction of Pd(II) to Pd(0) in 1-ethyl-3-methylimidazolium ethylsulfate ([C₂C₁Im][EtSO₄]) by XPS [23–25]. It not only opened the door for the analysis of ionic liquid-based solutions by XPS but provided with an opportunity to further understand the processes involved when a metal catalyst is dissolved in ionic liquids, *i.e.* the metal-ligand interaction and the solute-solvent interaction [26].

* Corresponding author at: School of Material Science and Engineering, Shenyang Ligong University, Shenyang 110159, PR China.

** Corresponding author.

E-mail addresses: menshuang@hotmail.com (S. Men), peter.licence@nottingham.ac.uk (P. Licence).

Since then, there have been lots of publications from all over the world focusing on the use of XPS to analyse ionic liquid-based metal catalytic systems [27,28]. In 2006, Maier et al. used angle resolved XPS (ARXPS) to analyse a platinum catalyst in $[\text{C}_2\text{C}_1\text{Im}][\text{EtSO}_4]$ and for the first time showed surface enrichment of the cation of the catalyst [29]. In 2008, Neatu et al. proved the chemical state of Au in an ionic liquid mixture using an XPS Au 4f high resolution spectrum together with Extended X-ray Absorption Fine Structure (EXAFS) measurements. In the same year, Nguyen et al. investigated the reduction of Fe in halometallate-based ionic liquids with the anions $[\text{FeCl}_4]^-$ and $[\text{Fe}_2\text{Cl}_7]^-$ [30]. In 2009, Tao et al. analysed the presence of Pd(II) nanoparticles in ionic liquid-based catalytic systems on sepiolite [31]. Shortly after, the Licence group monitored the *in situ* electrochemical generation of an Fe(III) species in an ionic liquid system using a special electrochemistry-XPS (EC-XPS) set up [32]. In 2010, the same group also investigated the *in situ* dissolution of copper into ionic liquids by EC-XPS [33]. Later in the same year, Kolbeck et al. investigated the ligand effect on the surface composition of Rh-containing ionic liquid systems by XPS [34]. In the same year, Apperley et al. analysed chloroindate-based ionic liquids by XPS together with EXAFS and found that there is indium chloride power suspended in the neutral tetrachloroindate ionic liquid [35]. Recent studies have highlighted that the XPS signals can act as reporters to tune the electronic environment of metal atoms in halometallate-based ionic liquids [36,37] and as probes of solvent–solute interactions in ionic liquid-based palladium systems [26,38].

In this study, we extend the use of XPS as an effective technique to investigate the rhodium–ligand interaction in ionic liquids. The ligand effect on the electronic environment at the rhodium centre of $[\text{Rh}(\text{acac})(\text{CO})_2]$ is explored. The formation of phosphine rhodium complex based upon the addition of phosphine ligands is confirmed by XP spectra. The influence of the basicity of the anion on the formation of different types of rhodium complexes is also investigated. The reaction selectivity of such catalytic system due to different types of metal–ligand interaction is correlated to the measured binding energies of Rh 3d_{5/2}.

2. Experimental methods

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. Lithium bis[(trifluoromethane)sulfonyl]imide was obtained from 3M and used as received. All ionic liquids investigated in this study were prepared in our laboratory using established synthetic protocols, $[\text{C}_8\text{C}_1\text{Im}][\text{OAc}]$ [39], $[\text{C}_8\text{C}_1\text{Im}]\text{Cl}$ [40], $[\text{C}_8\text{C}_1\text{Im}][\text{BF}_4]$ [41], $[\text{C}_8\text{C}_1\text{Im}][\text{TfO}]$ [42], $[\text{C}_8\text{C}_1\text{Im}][\text{PF}_6]$ [40], and $[\text{C}_8\text{C}_1\text{Im}][\text{Tf}_2\text{N}]$ [43]. The structures of the individual cations and anions investigated in this study are shown in Table S1.

Unless otherwise stated, all ionic liquids were characterised by ¹H and ¹³C NMR; spectra were recorded on a Bruker DPX-300 spectrometer at 300 and 75 MHz respectively as solutions in CDCl₃ and DMSO-d₆. When anion exchange was one of the synthetic steps, ion chromatographic analysis showed that halide concentration <10 ppm. No halide signal was observed by XPS analysis, *i.e.*, the concentration was below the limit of detection in every case. Full data for all materials studied in this work appears in the supplementary information.

2.2. Sample preparation

In this study, Rh-containing ionic liquid-based samples were prepared using PPh₃ and 1,1'-Bis(diphenylphosphino)ferrocene

(dppf) as ligands. Moreover, since the rhodium catalyst shows limited and slow solubility in ionic liquids, dichloromethane was added into the mixture to speed up solvation processes [44,45]. The addition of dichloromethane allows full contact of the catalyst and ionic liquids as they are both dissolved in dichloromethane. Dichloromethane can then be removed, firstly under rotary evaporator and then under high vacuum at room temperature for more than 12 h, to give Rh-containing ionic liquid based samples. It must be noted that the signal to noise ratio of the Rh 3d spectrum is relatively low when compared to the other spectra. This is due to the relatively low concentration of $[\text{Rh}(\text{acac})(\text{CO})_2]$ in the ionic liquid solution, *i.e.* lower than 0.02 atomic % in all cases.

2.3. XPS data collection

All XP spectra were recorded using a Kratos Axis Ultra spectrometer employing a focused, monochromated Al K α 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 × 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 × 10⁵ 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 (≈ 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 $\approx 0^{-7}$ 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 [46].

2.4. 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 $\cos \theta$, where θ is the electron emission angle relative to the surface normal.

Download English Version:

<https://daneshyari.com/en/article/5379359>

Download Persian Version:

<https://daneshyari.com/article/5379359>

[Daneshyari.com](https://daneshyari.com)