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Ligand Effects on the Surface Composition of Rh-Containing Ionic Liquid Solutions Used in Hydroformylation Catalysis

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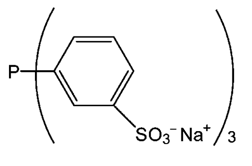
In hydroformylation, multiphase catalysis is a well-established and industrially realized[1] method for effective catalyst separation and recycling. Aqueous phase liquid–liquid biphasic catalysis was developed through the pioneering discovery of the highly water-soluble ligand tris(3-sodium sulfonatophenyl)phosphine (tppts, **1**) by Kuntz in 1976.[2]



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This ligand concept enabled the industrial realization of aqueous hydroformylation for propene hydroformylation in the Ruhrchemie–Rhône–Poulenc process. The process went on stream in 1984, and is still operating today (550000 tons per year).[3] However, the limited solubility of higher olefins ($>C_4$) in water has prompted much research activity into alternative polar catalyst media for liquid–liquid multiphase hydroformylation. Among these endeavors, the use of low-melting salts, so-called ionic liquids (ILs),[4] has attracted particular interest as many ionic liquids show sufficiently high solubilities for higher olefins to allow reasonable reaction rates.[5] First reports on the application of ionic liquids in Rh-catalyzed hydroformylation were published by Chauvin's group in 1995.[6] Already in this first paper, the use of sulfonated triphenylphosphine ligands was highlighted as a crucial precondition to avoid Rh-leaching into the organic product phase. Later, sulfonated triphenylphosphine ligands were also combined with imidazolium counter ions. Cole-Hamilton and co-workers suggested, for example, $[C_3mim]_2[PhP(C_6H_4SO_3)_2]$ as a suitable ligand for hydroformylation reactions in the biphasic system ionic liquid/$scCO_2$.[7]

The same ligand system was applied recently to an even more efficient catalytic system using the ionic catalyst solution in the form of a supported ionic liquid phase (SILP).[8] Such SILP catalytic systems have also been very successfully applied in continuous gas-phase reactions where the ionic liquid film supported on a highly porous inorganic support is contacted directly with the gas-phase of the reactants to perform continuous hydroformylation using a continuous fixed-bed reactor.[9] In general, hydroformylation in ionic liquids has produced a huge amount of scientific activity over the last 15 years and particular progress was made by the use of regioselective ionic ligand systems[10] and by the application of ionic liquids carrying halide-free, cheap and hydrolytic stable anions.[11] The field has been recently summarized comprehensively in an excellent review by Haumann and Riisager.[12]

In multiphase catalysis, interface processes such as substrate diffusion into the catalyst phase, the reaction rate at the phase boundary (in comparison to reaction rate in the bulk), and product diffusion back into the organic phase play a crucial role for the overall performance of the system. Despite this obvious fact, experimental investigations into the chemical nature of the liquid surface of catalytic systems are lacking so far. This is even more surprising in the light of recent theoretical findings by the group of Wipff,[13] which demonstrated that the composition of the catalytic interface may well be very different from the average chemical composition of two adjacent bulk liquid phases. This fact is of high relevance for the detailed understanding of all above-mentioned interface transport and reaction processes. Moreover, the authors demonstrated that the surface-active character of a given type of an IL soluble complex was similar at the IL–vacuum interface and at the IL interface with weakly polar organic solvents.[13b] The

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physico-chemical reason for the chemical composition of the near-surface region to be different from the bulk liquid is found in the unbalanced forces present at the liquid's surface due to its non-isotropic environment.

Over the last few years, our groups and others have started to study the chemical composition of the surface of ionic liquids on a molecular level.[14] Owing to the very low vapor pressure of ILs,[15] spectroscopic surface science techniques—formerly only applied to study solid surfaces—can be adopted to investigate IL surfaces. Examples include direct recoil spectroscopy (DRS),[14a,b] high-resolution electron energy loss spectroscopy (HREELS),[16] low-energy ion scattering (LEIS),[17] Rutherford back-scattering,[18] X-ray and neutron reflectometry,[19] and grazing incidence X-ray diffraction.[20]

In addition to these methods, X-ray photoelectron spectroscopy (XPS), also denoted as electron spectroscopy for chemical analysis (ESCA), has proven to be one of the most powerful methods to analyze the chemical composition of the near-surface region of ionic liquids. Since core level binding energies are sensitive to the local chemical environment, XPS allows the determination of the chemical state (e.g., oxidation state) of a particular atom in the near-surface region of an ionic liquid in a quantitative manner. Note that XPS is characterized by an inherent surface sensitivity originating from the low inelastic mean-free path of photoelectrons in the ionic liquid. This limited mean free path is also the basis for angle-resolved XPS (ARXPS), a technique that allows probing the surface of the ionic liquid with different information depth. With our experimental setup,[21] photoelectrons emitted elastically along the surface normal (i.e., in a more bulk sensitive geometry) originate from the first 7–9 nm of the ionic liquid, whereas photoelectrons with an 80° emission angle (i.e., in a more surface sensitive geometry) only probes the first 1–1.5 nm.[22]

It has been shown that the composition of ILs in the near-surface region can be quantified accurately by ARXPS[21] and contaminations[23] or surface-enrichment effects[24] can be safely identified and quantified. Also the surface compositions of a few ionic solutions, including dissolved transition-metal compounds, have been investigated.[14d,e] However, none of these latter systems was of immediate relevance for the better understanding of an industrially important catalytic reaction. Moreover, no attention was given to the influence of ligand effects on the composition of liquid catalytic surfaces in these former studies.

Herein we report for the first time an ARXPS study of ionic catalyst solutions containing dissolved Rh complexes and the tppts ligand as applied in multiphase hydroformylation catalysis. In detail, we present the influence of the tppts ligand on the Rh-catalyst concentration at the ionic liquid surface.

As starting point of our investigation we studied the solubility of $[Rh(acac)(CO)_2]$ and of the tppts ligand independently in various ionic liquids (Table 1). Note that all data presented in Table 1 have been obtained by maximizing solubility using a cosolvent-enhanced saturation method. For this, $[Rh(acac)(CO)_2]$ and tppts were first dissolved in acetonitrile (CH_3CN) and the ionic liquid was added to this solution. After complete removal of the acetonitrile, the Rh and phosphorus concentrations were determined by inductive plasma-coupled atomic absorption spectroscopy (ICP-AAS).

Table 1. Maximum solubility of $[Rh(acac)(CO)_2]$ and tppts in various ionic liquids as determined by ICP-AAS.

	Ionic liquid[a]	$[Rh(acac)(CO)_2]$ [mol %]	tppts [mol %]
1	$[C_2mim][Tf_2N]$	0.01	0.05
2	$[C_2mim][C_2H_5\text{-}OSO_3]$	0.19	16.1
3	$[C_2mim][C_8H_{17}\text{-}OSO_3]$	0.60	3.68
4	$[C_4mim][C_8H_{17}\text{-}OSO_3]$	2.89	2.21
5	$[C_2mim][PF_3(C_2F_5)_3]$	4.57	0.12

[a] $[C_2mim]$ = 1-ethyl-3-methylimidazolium, $[C_4mim]$ = 1-butyl-3-methylimidazolium.

Remarkably, $[Rh(acac)(CO)_2]$ shows high solubility in $[C_2mim]\ [PF_3(C_2F_5)_3]$ and $[C_4mim][C_8H_{17}\text{-}OSO_3]$, whereas tppts solubility peaks in $[C_2mim][C_2H_5\text{-}OSO_3]$ and is very low in all strongly hydrophobic ionic liquids (due to its own highly hydrophilic nature).

In a first set of ARXPS investigations we studied the Rh-containing IL solutions in the absence of any tppts ligand. Rh signals of the saturated solution of $[Rh(acac)(CO)_2]$ in $[C_2mim][C_2H_5\text{-}OSO_3]$ were found to be below the detection limit of XPS. This is understandable from the very low concentration of Rh in this solution (see Table 1, entry 2). Moreover, this result indicates that there is no extreme surface enrichment of Rh found in this ligand-free system. Investigation of a saturated solution of $[Rh(acac)(CO)_2]$ in $[C_4mim][C_8H_{17}\text{-}OSO_3]$ in contrast resulted in the spectra displayed in Figure 1.

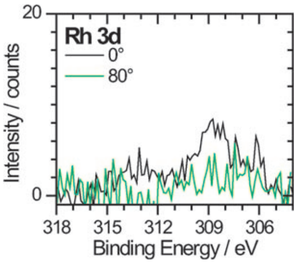


Figure 1. ARXP spectra of a saturated solution of $[Rh(acac)(CO)_2]$ in $[C_4mim][C_8H_{17}\text{-}OSO_3]$: Rh 3d region (0°: bulk sensitive, 80°: surface sensitive).

While the Rh concentration determined at a 0° emission angle determined by XPS (2.8 mol %) matches the average Rh concentration in the ionic liquid determined by ICP-AAS (2.89 mol %; Table 1, entry 4) very well, almost no Rh is found for an 80° emission angle, indicating that the top layer of the ionic liquid film is virtually free of Rh. This behavior becomes understandable from the known fact that long alkyl chain substituents, like the octyl group of the octylsulfate anion, are enriched at the ionic liquid's surface.[24b]

Thus, this ionic liquid forms a highly apolar surface region, in which Rh is largely depleted.

To study the influence of the tppts ligand on the surface composition of ionic liquids, we first studied a ligand-saturated solution of $[C_2mim][C_2H_5\text{-}OSO_3]$ without added Rh. Figure 2a and b show the C 1s and Na 1s spectra, respectively, for a 0° and 80° emission angle.

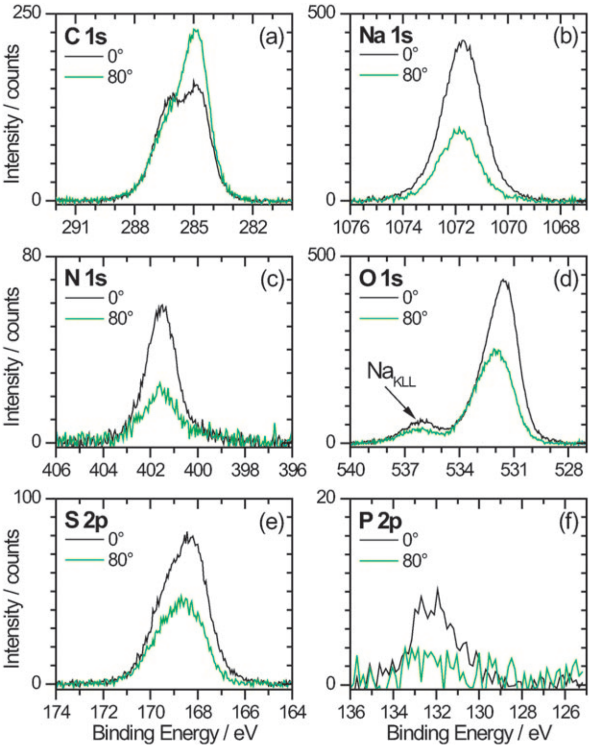
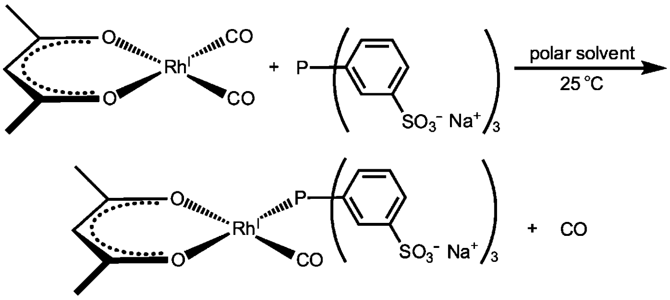


Figure 2. ARXP spectra of a saturated solution of the tppts ligand (16.1 mol%) in $[C_2mim][C_2H_5\text{-}OSO_3]$; a) C 1s, b) Na 1s, c) N 1s, d) O 1s, e) S 2p, f) P 2p regions. In (d) the position of the Na KLL Auger signal is indicated.

The C 1s spectra clearly indicate that the tppts ligand shows a very high surface affinity. The C 1s peak corresponding to the aromatic carbon of the ligand (285.0 eV) strongly increases for an 80° emission angle compared to a 0° emission angle. In contrast, the C 1s peak at 286.5 eV, which is dominated by the ionic liquid's heterocarbon atoms, shows a relative decrease by going from a 0° to an 80° emission angle. Interestingly, the Na 1s spectra give some additional insight into the surface orientation of the tppts ligand dissolved in the ionic liquid. As seen from Figure 2b, Na^+ ions are strongly depleted from the top 1–1.5 nm (80° spectrum) of the ionic liquid surface. A similar behavior was also observed for the S 2p and O 1s signals (Figure 2d and e, respectively), confirming our expectation that the Na^+ ions are attached to the ionic SO_3^- groups of the ligand. The depletion of the P 2p signal at 80° (Figure 2f) indicates that the P atoms are also not located at the outer surface. These spectroscopic findings lead to a picture in which the surface is dominated by the tppts ligand in an oriented manner. While the nonpolar phenyl groups are pointing towards the vacuum, the P atom and the SO_3^- groups in the *meta* position are directed towards the bulk of the ionic liquid. The much lower 80° intensity of the N 1s signal, which is the only signal that can solely be attributed to IL cations, confirms the depletion of the IL at the outer surface, due to the enrichment and preferential orientation of the tppts ligand. This picture is in line with the general trends obtained by the theoretical calculations of Sieffert and Wipff.[13] It is known from the literature that the $[Rh(acac)(CO)_2]$ precursor reacts in polar solvents with the tppts ligand at room temperature according to Scheme 1.[25]



Scheme 1. Reaction of Na_3tppts with $[Rh(acac)(CO)_2]$ in polar solvents (according to ref. [25]).

The same reaction can be expected in ionic liquids. Indeed, when adding $[Rh(acac(CO)_2]$ to a saturated solution of tppts in $[C_2mim][C_2H_5\text{-}OSO_3]$, a maximum concentration of 5.1 mol% Rh in the IL is achieved compared to 0.19 mol% (Table 1, entry 2) in the same ionic liquid without the tppts ligand. This induced increase of the Rh concentration by a factor 27 is a strong indication for the in situ transformation of the Rh complex in the polar ionic liquid solution by the coordination of the tppts ligand in the same way as shown in Scheme 1. Figure 3a–g display the Rh 3d, C 1s, Na 1s, N 1s, O 1s, S 2p, and P 2p spectra, respectively, of the so obtained ionic liquid/Rh–tppts complex solution.

The Rh 3d spectra in Figure 3a show the expected 5.1 mol% Rh concentration in the bulk-sensitive 0° emission angle measurement. Remarkably, the increase in relative and also in absolute intensities (note the scales in Figures 2a vs. 3b) of the phenyl C 1s signal at about 285 eV, when going from 0° to 80° emission (Figure 3b), is even more pronounced than without the presence of the Rh precursor. This behavior indicates that, in addition to non-reacted (ca. 2/3) ligand with their phenyl groups pointing towards the vacuum, phenyl rings from the in-situ-formed Rh complex are also present at the surface. Thus, the overall increase of phenyl rings at the outer surface clearly reveals surface enrichment of the in-situ-formed Rh complex. All other signals (Figure 3b–g) display a decrease at 80°, which demonstrates that the SO_3 groups and the P atoms of both the unreacted tppts ligand and the in-situ-formed complex again preferen-

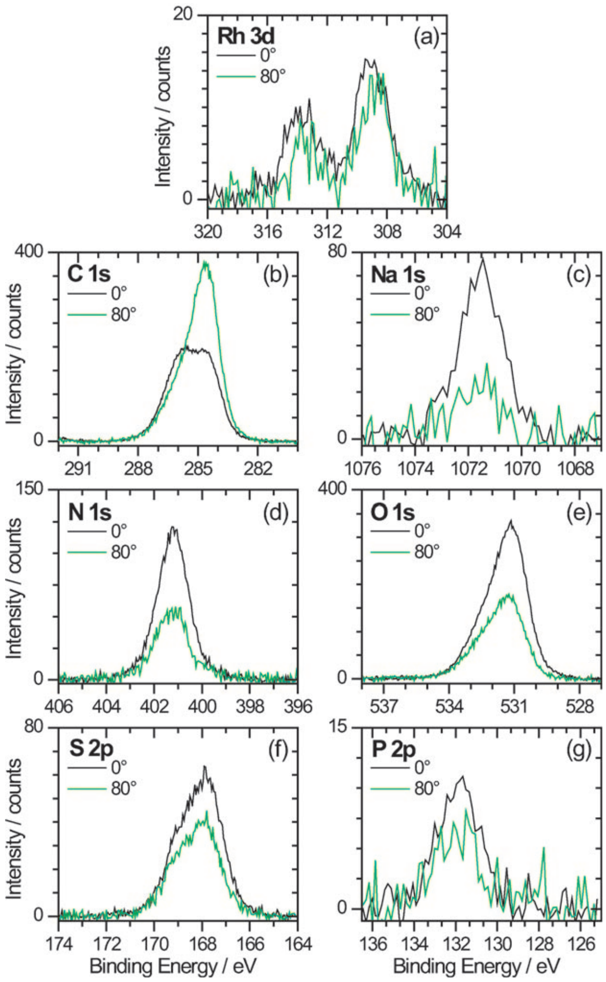


Figure 3. AR-XP spectra of a saturated solution of tppts in [C_2mim][C_2H_5-OSO_3] with 5.1 mol% [Rh(acac)$(CO)_2$] dissolved: a) Rh 3d, b) C 1s, c) Na 1s, d) N 1s, e) O 1s, f) S 2p, and g) P 2p regions.

tially point towards the bulk of the IL. Also, the IL components are depleted from the outermost surface layer.

Interestingly, the Rh signal intensity remains nearly constant when going from a 0° to an 80° emission angle. Given that the Rh atoms in the in-situ-formed Rh–tppts complex are not expected at the outer surface and thus experience damping by the surface phenyl groups in the 80° measurement, this is in line with the surface enrichment of the in-situ-formed complex. Furthermore, the stronger increase of the phenyl C 1s signal (ca. 285 eV) and the weaker decrease of the P 2p signal at 80° as compared to the Rh-free system (Figure 3 vs. 2) indicates that the enrichment of the in-situ-formed complex is even more pronounced than that of the tppts ligand. Thus, our findings clearly result in a chemical surface composition of this catalyst solution for hydroformylation catalysis that is characterized by a significant and even slightly preferred presence of the Rh–tppts complex in the top 1–1.5 nm of the catalytic ionic liquid.

The strong overall decrease of the Na 1s signal by a factor of about 5 (Figure 3c vs. Figure 2b), which accompanies an overall increase of the imidazolium-based N 1s signal (Figure 3d vs. Figure 2c) indicates a significant depletion of Na^+ ions in the top layer of the complex solution compared to the Rh-free system, that is, the solvation of the SO_3^- groups of the tppts ligand by counter cations is strongly altered in the near-surface region when the Rh–tppts complex is formed.

In conclusion, we demonstrate for the first time experimentally that the nature of the applied ligand influences the preferred position of the catalyst complex in either the bulk phase or at the interface of a multiphase catalytic system. The highly application-relevant Rh–tppts complex proved to exhibit significant surface activity in the ionic liquid [C_2mim][C_2H_5-OSO_3], whereas the tppts-free system with the same Rh precursor [Rh(acac)$(CO)_2$] shows even Rh depletion from the surface. With these results we provide spectroscopic evidence for results from molecular dynamics studies by Sieffert and Wipff who claimed significant interface (surface) activity of Rh–tppts complexes in organic/ionic liquid (vacuum/IL) multiphase systems.[13] In general our study allows a more complete view on multiphase homogeneous catalyzed reactions. As maximizing the catalyst concentration at the phase boundary is a very attractive strategy for the optimization of these reactions (e.g. reduction of mass transfer limitations, faster reaction of weakly soluble substrates, beneficial selectivity effects due to the non-isotropic catalyst environment), we anticipate that our findings will encourage targeted attempts to manipulate the surface activity of transition-metal complexes in multiphase catalytic systems.

Experimental Section

All solubility measurements were performed under an inert atmosphere of argon using standard Schlenk-tube techniques. Catalyst, ligand, and solvent were purchased from Strem Chemicals or Aldrich. Catalyst (0.04 g) or ligand (0.30 g) and IL (1.0 mL) were stirred in acetonitrile for 24 h at room temperature. After evaporation of the solvent the saturated solution was prepared for the analysis of solute composition. The total rhodium, phosphorus, sulfur, or sodium content of the solutions was determined by ICP-AAS after dissolution of the samples in ethanol using a Spectro ciros ICP-AAS spectrometer. Sample preparation for ARXPS and XPS parameters were reported previously.[24]

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Keywords: ionic liquids · multiphase catalysis · photoelectron spectroscopy · P ligands · surface science

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