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Controlling the activity and selectivity of polymerised ionic liquids-stabilised ruthenium nanoparticles through anion exchange reactions

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ABSTRACT: The development of highly active and selective heterogeneous-based catalysts with tailorable properties is not only a fundamental challenge, but is also crucial in the context of energy savings and sustainable chemistry. Here, we show that ruthenium nanoparticles (RuNPs) stabilised with simple polymerised ionic liquids (PILs) based on N-vinyl imidazolium led to highly active and robust nano-catalysts in hydrogenation reactions, both in water and organic media. Of particular interest, their activity and selectivity could simply be manipulated through counter-anions exchange reactions. Hence, as a proof of concept, the activity of RuNPs could be reversibly turned on and off in the hydrogenation of toluene, while in the case of styrene, the hydrogenation could be selectively switched from ethylbenzene to ethylcyclohexane upon anion metathesis. According to X-Ray photo-electron spectroscopy (XPS) and Dynamic light scattering (DLS) analysis, these effects could originate from the relative hydrophobicity and solvation of the PIL corona but also from the nature and strength of the PIL-Ru interactions.

Introduction

The development of highly active, selective and recyclable catalysts is crucial in the context of energy savings and sustainable chemistry.^{1–7} Metallic nanoparticles (MNPs) are promising candidates because of their unique properties that stem from their nanometric size and the presence of high-energy surface atoms.^{8–13} As MNPs prove thermodynamically unstable respective to bulk metal, stabilisers such as polymers, ligands, surfactants or ionic liquids (ILs) are required to ensure colloidal stability.^{14–18} In addition, stabilisers may also strongly influence the catalytic properties of MNPs, owing to their multiple interaction with the MNPs surface.^{19–25} In this regard, polymeric stabilisers generally lead to highly stable dispersion of MNPs thanks to their steric protection.^{26–29} Meanwhile, steric congestion may limit the access of substrates to the surface, thus decreasing catalytic performances. In contrast, with molecular ILs as stabilisers, very active MNPs are formed.^{30–33} Nevertheless, such dispersions remain poorly stable under forcing conditions,³³ which can be overcome by adding some polymer.³⁴

Polymerised ionic liquids (PILs) are polymeric versions of ionic liquids (ILs), where cations (or anions) are tethered to the

polymer backbone and counter-ions are mobile.^{35–39} This class of poly(electrolytes), which combines the properties of polymers with those of ILs, behaves as powerful electro-steric stabilisers for MNPs.^{40–44} Hence, PILs, notably those based on the imidazolium cation, generally lead to PILs-stabilised MNPs catalytic systems, denoted as M@PIL NPs, with enhanced activity and improved stability relative to molecular IL-stabilised MNPs.⁴³ Applications of M@PIL NPs-type catalysts (M = Rh, Pd, Pt, Ni, Au and Ag) have proven efficient in a variety of chemical transformations, including Suzuki,^{45–50} Sonogashira,⁵¹ Heck^{49,50,52} and Stille⁴⁹ C-C couplings, as well as hydrogenation reactions.^{40,43,44,53–59}

Besides these outstanding stabilising properties, a peculiar advantage of PILs over more conventional stabilisers relies on the facile and reversible tuning of their physical and chemical properties by anion exchange (so-called anion metathesis) reactions. For instance, we have reported that unreactive poly(imidazolium)s could be transformed into reactive PILs thanks to the introduction of basic counter-anions by anion exchange.^{60–62} The resulting poly(imidazolium)s behave as masked poly(N-heterocyclic carbenes) for the purpose of organic catalysis and for post-functionalization as well. Furthermore, the solubility of PILs can be switched from aqueous to organic medium, and *vice versa*, by this simple counter-anions metathesis reaction.^{63,64} By analogy, when coated on MNPs, PILs allow the solubility of M@PIL NPs to be tuned; likewise their reversible transfer from water to an organic solvent has been reported.^{56,65}

As the adsorption of anions on metallic surfaces has been shown to affect the catalytic activity and selectivity of MNPs,^{66–70} we hypothesised that counter-anions exchange reactions

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could be harnessed to tailor the catalytic properties of PILs-stabilised MNPs (Figure 1 et 2).

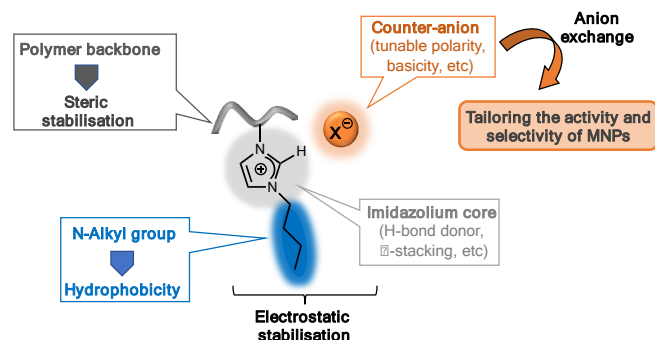


Fig. 1 Features of imidazolium-based PIL to manipulate the catalytic properties of MNPs.

We wish to report herein that simple PILs based on poly(1-butyl-3-vinyl imidazolium), associated with different anions, such as Cl, Br, I, bis(trifluoromethyl)sulfonimide (NTf₂) act as very efficient stabiliser for RuNPs both in water and organic media. More importantly, their catalytic activity can be tuned by simple counter-anions exchange reactions (Figure 2). Hence, this effect provides an innovative and powerful means to reversibly turn the catalytic activity of RuNPs on and off. Switching the chemo-selectivity of Ru@PIL NPs in the hydrogenation of styrene from ethylbenzene to ethylcyclohexane can also be accomplished upon I[−]/NTf₂[−] anion exchange (Figure 2). On the basis of XPS and DLS analysis, this anion effect could result from the specific interactions between the counter-anions and/or the imidazolium moieties of the PIL stabiliser and the Ru surface, as well as from the relative solvation and hydrophobicity of the PIL corona.

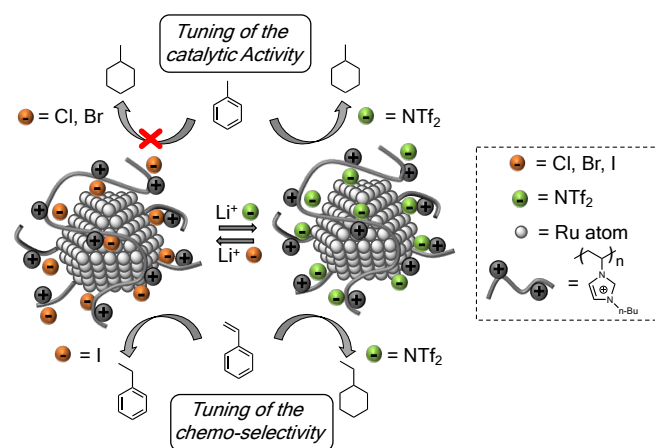


Fig. 2 Tuning the activity and selectivity of polymerised ionic liquid-stabilised Ru nanoparticles by anion exchange. NTf₂ -bis(trifluoromethyl)sulfonimide.

Results and discussion

The ability of poly(1-Butyl-3-vinyl-imidazolium chloride), denoted as PIL(Cl), to stabilise RuNPs was first investigated. PIL(Cl) was prepared by free radical polymerisation of the

corresponding N-vinyl imidazolium chloride ionic liquid monomer at 70°C in *iso*-propanol. The corresponding Ru@PIL(Cl) NPs were synthesized by a polyol process (Fig. 3),⁷¹ that is by reduction of RuCl₃ in ethylene glycol at 170 °C, in presence of different amount of PIL(Cl) (for details, see SI).

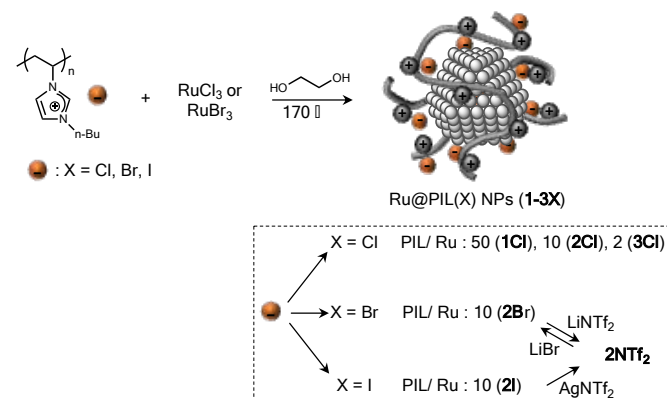


Fig. 3 Preparation of PIL(X)s-stabilised RuNPs (1-3X) by polyol process and anion exchange reactions (X = Cl, Br, I, NTf₂).

Using a PIL(Cl)/Ru molar ratio of 50, 10 and 2, mono-disperse NPs of 1.5 nm (**1Cl**), 2.6 nm (**2Cl**) and 2.7 nm (**3Cl**) were formed respectively, according to TEM analysis (Fig. 4). XRD analysis revealed that **1Cl**, **2Cl** and **3Cl** were polycrystalline, the size of the crystalline domains, as determined from the Debye-Scherrer relation, being much smaller than the size measured by TEM (1.1 nm, 1.3 nm and 1.4 nm for **1Cl**, **2Cl** and **3Cl** respectively; see Table S4). As an assessment of their stability in water, ζ-potential was then determined. All Ru@PIL(Cl) NPs exhibited positive values as expected from their poly-cationic nature (Fig. 4d). The ζ-potential also increased with the PIL/Ru ratio in the order **3Cl** (35 mV) < **2Cl** (49 mV) < **1Cl** (56 mV), indicating the higher stability of **1Cl**. The Ru(0) and Ru(IV) contents could be evaluated to 88% (BE = 461.4 eV) and 12% (BE = 463.4 eV) by XPS analysis of **2Cl** upon deconvolution of the Ru 3p3/2 signals (Fig. S18, Table S7).

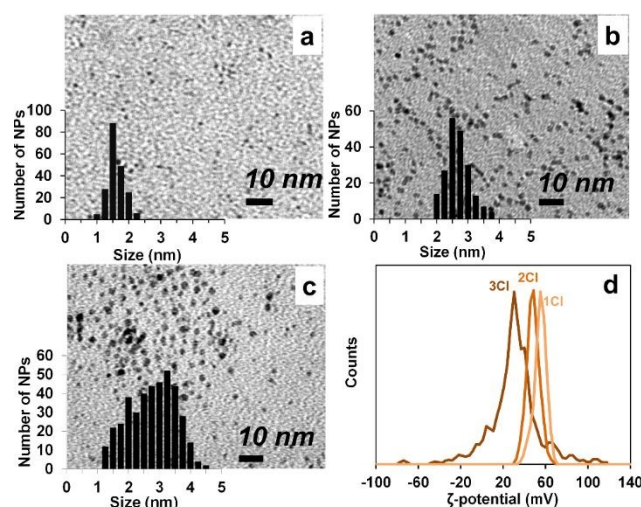
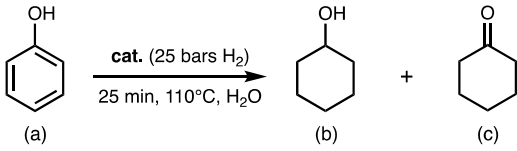


Fig. 4 TEM image and size histogram of (a) **1Cl**, (b) **2Cl**, (c) **3Cl** and (d) Zeta potential of **1-3Cl** in water at 25 °C.

To investigate the influence of the PIL counter-anions on the RuNPs catalytic properties, different Ru@PIL NPs with Br, I and NTf₂ anions were also prepared. **2Br** and **2I** were generated in a similar way as **2Cl**, using PIL(Br) and PIL(I) as stabilisers respectively, with a PIL(X)/Ru ratio equal to 10. In contrast, **2NTf₂** was accessed by anion metathesis between **2Br** and LiNTf₂ because of the insolubility of PIL(NTf₂) in ethylene glycol (Fig. 2). Importantly, no trace of residual bromide was detected in **2NTf₂** by XPS analysis (Fig. S14 & S15), evidencing that the anion exchange was quantitative. Alternatively, **2Cl** could be used instead of **2Br** for the anion metathesis, the anion exchange being also complete in this case (Fig. S15b). The size of the RuNPs was not affected by the anion exchange reaction but was found to decrease in the order: **2Cl** (2.6 nm) > **2Br/2NTf₂** (2.3 nm) > **2I** (1.6 nm) according to TEM analysis, highlighting the influence of the PIL counter-anions over the NPs size (Fig. S5 and S6). Although the origin of this effect is not clearly understood, it may result from the nature and intensity of the PIL/Ru and cation/anion interactions (*vide infra*).

Table 1. Hydrogenation of phenol in water catalysed by RuNPs.

			
Entry	NP	Conversion (%)	Selectivity (b %)
1	1Cl	62	88
2	2Cl	100	100
3	3Cl	100*	100
4	2Br	100	100
5 ^a	Ru@IL	100*	100
6 ^b	Ru@PVP	100*	100

Hydrogenation were performed with 0.166 mol.% of Ru catalyst and 6 wt% of phenol in 5 mL of water, at 110 °C, under 25 bars of H₂. The conversion was determined by ¹H NMR. The selectivity was confirmed by GC-MS analysis.

*Aggregation of NPs and/or bulk metal formation was observed. ^aIL: 1-butyl-3-ethyl-imidazolium bromide. ^bSee SI for their preparation and characterization.

Hydrogenation of phenol with Ru@PIL(X) NPs in water (X = Cl, Br)

The catalytic activity of **1-3Cl** was first investigated for the hydrogenation of phenol in water as model reaction (Table 1).⁷² Reactions were performed at 110 °C for 25 min, using 25 bars of H₂ and 0.166 mol.% of Ru loading. Under those conditions, **2Cl** appeared as the most efficient catalyst, providing full substrate conversion, as well as complete selectivity in favour of cyclohexanol (entry 2). In comparison, **1Cl** and **3Cl** displayed a moderate conversion (62 %, entry 1) and a poor stability (entry 3), respectively, highlighting that an intermediate ratio PIL/Ru ratio of 10 was the optimal balance. The same ratio was thus kept throughout the study. The formal replacing of Cl⁻ by Br⁻ had virtually no influence on the catalytic properties of such Ru@PIL(X) systems, as indicated by the full substrate conversion and full selectivity toward cyclohexanol obtained with **2Br**, under similar conditions (entry 4). For comparison purpose, RuNPs either electrostatically stabilised by an homologous monomeric ionic liquid, namely, 1-Butyl-3-

ethylimidazolium bromide, or sterically stabilised with neutral PVP were prepared by the same polyol process (see part 2b in SI), yielding to water-dispersible RuNPs of 1.8 and 2.7 nm respectively. In both cases, aggregation of the NPs and bulk metal formation were observed (Table 1, entry 5 and 6) under the standard conditions (110 °C, 25 min, 25 bars of H₂). In contrast, **2Br** and **2Cl** remained perfectly stable.

The recyclability of Ru@PIL NPs was also briefly examined. Quantitative phenol conversion could thus be achieved over 7 cycles with **2Cl**, without any sign of NP aggregation according to TEM analysis (Fig. S24 & S25). Although hydrogenation of aromatics generally involves heterogeneous species as catalysts, a CS₂ poisoning experiment was performed to confirm the heterogeneous nature of the catalyst.⁷³ Thus, upon addition of CS₂ to the catalytic solution containing **2Cl**, no further increase of the conversion with time was noted (Fig. S26), in agreement with a surface-mediated catalysis.

Switching of the catalytic activity by anion exchange

As Ru@PIL(X)NPs (**2Cl**, **2Br**, **2NTf₂** and **2I**) display different solubility depending on the type of counter-anions introduced, methanol was selected as common solvent to compare their catalytic activity under semi-heterogeneous conditions. Hydrogenation reactions were performed at 110 °C for 1 h, using 25 bars of H₂ and phenol as substrate. Under those conditions, **2I** proved completely inactive, while **2Br**, **2Cl** and **2NTf₂** afforded low substrate conversion of 2, 6 and 11% respectively (Table 2).

Table 2. Influence of PIL counter-anions over the catalytic activity of Ru@PIL(X) NPs (X = Cl, Br, I, NTf₂) for the hydrogenation of phenol and toluene.

Entry	NP	Phenol Conversion (%)	Toluene Conversion (%)
1	2Cl	6	10
2	2Br	2	2
3	2I	0	0
4 ^a	2NTf ₂	11	70
5 ^b	2Br ^c	-	5

Hydrogenation of phenol and toluene (6 wt% in 5 mL of methanol) were performed at 110 °C for 60 min using 0.33 mol.% of Ru catalyst and 25 bars of H₂. In all cases, conversion was determined by GC-MS. ^a2NTf₂ was prepared by anion exchange of **2Br** with LiNTf₂. ^b2Br^c was prepared by anion exchange of **2NTf₂** with LiBr.

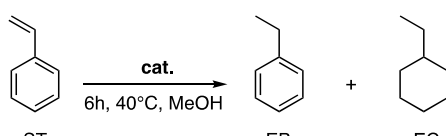
Although higher conversion was observed upon Br/NTf₂ anion exchange (2 and 11% for **2Br** and **2NTf₂** respectively, see entries 2 and 4), phenol conversion remained very low regardless of the catalyst. Toluene was next tested to evaluate the influence of the PIL counter-anions in the case of hydrophobic substrates. Here again, under the same experimental conditions, **2I** proved completely inactive, while **2Cl** and **2Br** afforded 10 and 2% of methylcyclohexane respectively (Table 2). To our delight, **2NTf₂**, resulting from a Br/NTf₂ anion exchange, provided 70% of conversion. Thus, the simple replacement of the hydrophilic bromide by the hydrophobic and weakly coordinating NTf₂ anion allowed the catalytic activity to be dramatically increased in the case of toluene. Remarkably, this process is reversible as the addition of LiBr to **2NTf₂** turned the catalyst back to its

inactive form **2Br'** (conv. ~ 5%) (Fig. S27). However, in contrast to the Br⁻/NTf₂⁻ anion exchange, 8% of NTf₂⁻ remained in **2Br'** according to XPS analysis (Figure S17), highlighting that the exchange was incomplete in this case. Thus, the catalytic activity of Ru@PIL(X) NPs could be switched on and off thanks to the reversible exchange of the PIL counter-anions. Although the influence of some anions over the catalytic properties of MNPs has been reported,⁶⁹ this anion exchange-mediated reversible switching of the catalytic activity is unprecedented to the best of our knowledge. This reversible behaviour originates from the specific properties of the PIL stabilisers, which combine a macromolecular structure and multiple, relatively weak anion-cation interactions. As already reported for other MNPs, this anion exchange reaction also allows the polarity of the catalysts to be readily modified (Table S2),^{56,65} leading to quantitative hydrogenation of toluene with **2NTf₂** as catalyst in THF as solvent (Table S10).

Switching of the catalytic selectivity by anion exchange

The inability of **2I** to hydrogenate aromatics (Table 2), prompted us to investigate the selective hydrogenation of C=C bonds using styrene as model substrate (Table 3). Thus, hydrogenation of styrene was performed at 40 °C under 15 bars of H₂, in presence of a catalytic amount of **2I** (0.33 mol% of Ru). Under these conditions, we were pleased to observe full substrate conversion and complete selectivity for ethylbenzene (EB) (Table 3, entry 2).

Table 3. Hydrogenation of styrene (ST) to ethylbenzene (EB) and ethylcyclohexane (EC) using Ru@PIL(X) NPs (X = Br, I, NTf₂) as catalysts.

			
Entry	NP	Conversion (%)	EB/EC selectivity (%)
1	2Br	100	64/36
2	2I	100	100/0
3	2NTf₂ ^a	100	0/100
4	Ru/C (5%) ^b	100	16/84

Hydrogenation in methanol (5 ml methanol and 6 wt% of styrene) at 40 °C for 6 hours under 15 bar of H₂ and 0.33 mol.% of Ru loading. GC-MS was used to determine conversion and chemo-selectivity of different catalysts. ^a**2NTf₂** was prepared by anion exchange between **2I** and AgNTf₂. ^bCommercial catalyst.

In the case of **2Br**, styrene was fully converted into a mixture of 64% of EB and 36% of ethylcyclohexane (EC), highlighting a lack of chemo-selectivity in this case. In sharp contrast, when **2NTf₂** was used under identical conditions, both the vinyl group and the aromatic ring were quantitatively reduced (entry 3). Interestingly, **2NTf₂** could be generated from **2I** using AgNTf₂ (SI Sec. 2c), which enabled the chemo-selective hydrogenation of styrene to be switched from EB to EC, upon I⁻/NTf₂⁻ anion exchange, while maintaining quantitative conversion (Fig. S16). For comparison, hydrogenation of styrene was also performed with Ru/C (5%) under the same conditions, leading to a mixture

of EB (16%) and EC (84%) (Entry 4), and thus evidencing the superior selectivity of Ru@PIL(X) NPs. Overall, those results not only demonstrated the interest of Ru@PIL(X) NPs catalytic systems relative to commercial catalysts, but also further highlighted the influence of PIL counter-anions over the catalytic properties.

Investigation of the PIL(X)-RuNPs interactions in the solid state

To gain more insight into the influence of the nature of PILs on NP properties, XPS analysis was performed on all Ru@PIL(X) NPs, i.e. **2Cl**, **2Br**, **2I** and **2NTf₂** (prepared from **2Br** by anion exchange), as well as on corresponding PIL(X) stabilisers (X = Cl, Br, I, NTf₂; Fig. 5). Although this analysis is performed in the solid state, it provides qualitative information on the nature and relative strength of PIL-Ru interactions.

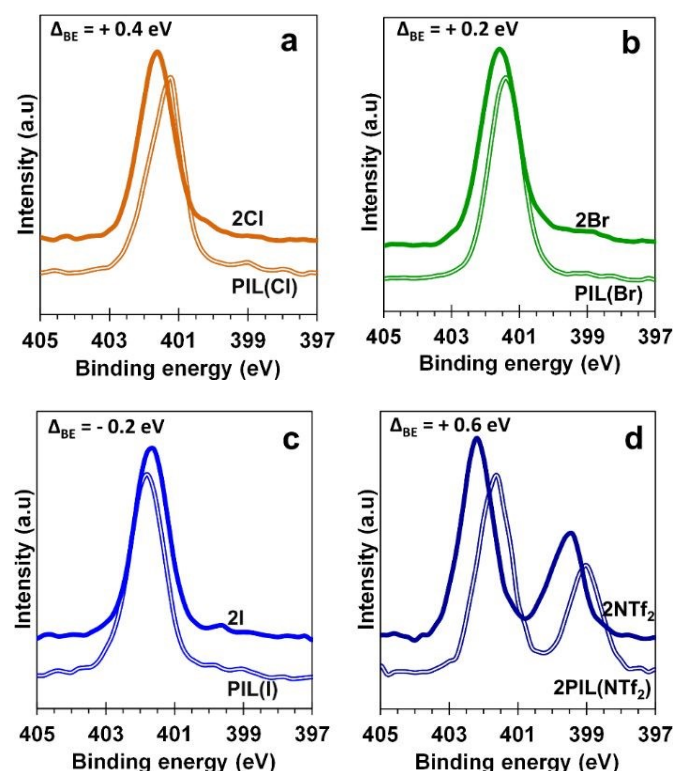


Fig. 5 Overlay of high resolution XPS scans in N(1s) region showing (a) PIL(Cl) and **2Cl**, (b) PIL(Br) and **2Br**, (c) PIL(I) and **2I** (d) PIL(NTf₂) and **2PIL(NTf₂)**.

Except iodide (I⁻), all anions were found to interact with the Ru surface as evidenced by the shift toward higher binding energy (BE) of the signals associated to Cl(2p), Br(3p), N(1s)NTf₂ compared to their respective BE in the free polymer (Fig. S21). More specifically, the strongest interaction with the Ru surface was observed for both Br and NTf₂ anions (ΔBE = +0.4). In the case of I⁻, no detectable shift in the BE I(3d) was observed between PIL(I) and the corresponding RuNPs **2I**, suggesting the absence of interaction between I⁻ and the Ru surface.

The environment around the imidazolium cation was next scrutinized by analysing the BE of the N(1s)Im. In the free PIL(X), anions interact solely with imidazolium cations, likely by H-bonding with the C₂-H and C_{4,5}-H.⁷⁴ The BE N(1s)Im was found to increase with an increase of the polarizability of the anion in

the order: Cl (401.2 eV) < Br (401.4 eV) < NTf₂ (401.6 eV) < I (401.8 eV) (Fig. 5a-d and Table S8). Thus, the most polarizable NTf₂⁻ and I⁻ anions only weakly interact with the imidazolium cation, leading to a cationic structure, where the electrons are tightly bound to the N atom. In contrast, the low BE N(1s)Im observed for Cl reflects its strong interaction with the imidazolium moiety via H-bonding, which virtually led to a partial transfer of the positive charge from the nitrogen atom to the proton.

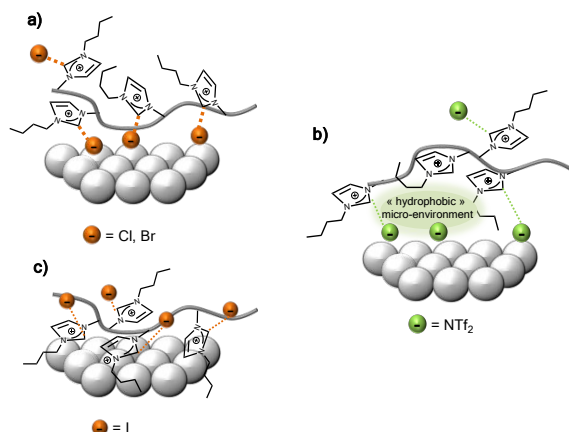


Fig. 6 Schematic representation of the interaction between PIL(X) and the Ru surface with (a) PIL(X=Cl or Br), (b) PIL(NTf₂) and (c) PIL(I).

In Ru@PIL(X) NPs (X= Cl, Br and NTf₂), the signal corresponding to N(1s)Im was shifted to higher BE relative to that of their respective PIL(X), indicating a weakening of the anion-cation interactions in presence of Ru. This effect was more pronounced for **2NTf₂** (Δ_{BE} = +0.6) than for **2Cl** (Δ_{BE} = +0.4) and **2Br** (Δ_{BE} = +0.2) (Fig. 5a, b and d and fig. 6a,b). In sharp contrast, a 0.2 eV shift toward lower BE was noted for the N(1s)Im of **2I**, relative to that of PIL(I) (Fig. 5c), suggesting an interaction between imidazolium cations and the Ru surface (Fig. 6c).^{75,76} From a catalysis point of view, such interactions would prevent aromatic substrates from adsorbing onto the flat surface of faces and to undergo hydrogenation of the aromatic moiety (fig. S23), as observed experimentally with **2I** and toluene and styrene as substrates. However, binding of styrene *via* the alkene moiety to edges or corners of RuNPs would not be hindered,^{8,77,78} allowing for complete EB selectivity with **2I** as catalyst. Note also that the smaller size of **2I** relative to **2Cl** and **2Br** observed by TEM (Fig. S5) may also originate from this peculiar imidazolium-Ru interaction, which would inhibit NP growth during their synthesis.

Influence of the PIL counter-anions (X) over the properties of Ru@PIL(X) NPs in solution

Dynamic light scattering (DLS) was performed on **2Br**, **2NTf₂** and **2I** in MeOH in order to investigate the influence of the counter-anions over the solution properties of NPs. The intensity-weighted size distributions were found to be bimodal for **2Br** and **2NTf₂**, suggesting the presence of some aggregation that likely resulted from inter-particular hydrogen bonding between imidazolium cations and respective counter-anions (fig. 7a).⁷⁴ However, the number-weighted size distributions of **2Br** and

2NTf₂ indicated that the proportion of these aggregates was very small, a single population at 8 and 12 nm, corresponding to isolated NPs, being observed for **2Br** and **2NTf₂** respectively (fig. 7b).

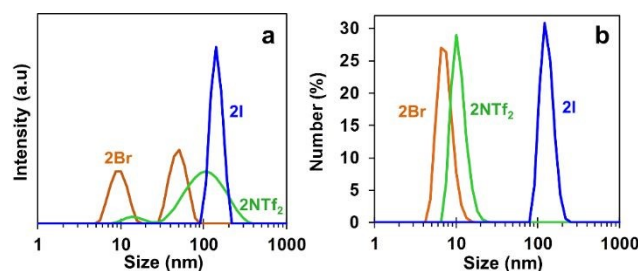


Fig. 7. DLS of **2Br**, **2NTf₂** and **2I** shown in (a) intensity-weighted size distributions and (b) number-weighted size distributions.

In contrast, only aggregates of about 180 nm were observed for **2I** on both types of size distribution (fig. 6a, b), which could result from the peculiar binding mode of PIL(I) to Ru that involves interactions between the poly(cationic) chains and the Ru surface, as demonstrated by XPS analysis (fig. 6c).

All these data clearly evidenced that the nature of PILs counter-anions has a dramatic impact on the nature and strength of the PIL-Ru and anion-cation interactions, both in the solid state and in solution. While the selectivity observed with **2I** could originate from the peculiar imidazolium-Ru interaction, the higher activity of **2NTf₂**, relative to **2Br**, in the hydrogenation of toluene and styrene could be ascribed to a more favourable micro-environment due to the better solvation of the PIL corona on one hand (Fig. 7b), and, on the other hand, to the relative hydrophobicity due to the presence of n-butyl substituents on imidazolium units and NTf₂⁻ counter-anions (Fig. 6b).

Conclusions

Easily accessible imidazolium-based polymerised ionic liquids (PILs) behave as powerful electro-steric stabilisers for RuNPs, affording highly active systems for the hydrogenation of aromatic substrates in different solvents such as water, MeOH or THF. In comparison to more conventional stabilisers, PILs provide a tailorable micro-environment around the metallic surface, which enable for reversibly controlling the catalytic properties of the corresponding RuNPs by simple exchange of the PIL counter-anions. Hence, this strategy allows, not only the catalytic activity to be turned on and off, but also the chemo-selectivity of RuNPs to be switched depending on the nature of the counter-anions. According to XPS and DLS analysis, influence of the PIL over the activity and selectivity of RuNPs stems from the relative hydrophobicity and solvation of the PIL corona and from the nature (via the anion or the cation) and strength of PIL-Ru interactions, respectively. Overall, this work demonstrates that, conceptually, different activity and selectivity can be reached from a single catalyst through anion exchange reactions. The variety of cations and anions available offers a bright horizon to tailor the metal surface properties of

MNPs, via simple anionic metathesis. Future work is underway to extend this concept to other poly(electrolyte)s and other metals, for a wide range of transformations.

Experimental and methods

Preparation of poly(ionic liquid)s (PILs) and Ru@PIL(X) NPs

Polymerised ionic liquids PIL(X) (X = Cl, Br, I) were prepared by free radical polymerisation of the corresponding 1-butyl-3-vinyl-imidazolium ionic liquid (ILs) monomers at 70 °C for 24 h, using AIBN as initiator (IL/AIBN = 200). ¹H NMR analysis after polymerisation confirmed 100% conversion of IL(Cl) and IL(Br). Conversion of 75% was obtained in the case of IL(I) after 48 hours of polymerisation. Poly(1-Butyl-3-vinylimidazolium chloride) (PIL(Cl)) and Poly(1-Butyl-3-vinylimidazolium bromide) (PIL(Br)) were precipitated repeatedly in diethyl ether and dried under vacuum (35 °C) till a constant weight was obtained (quantitative yields). PIL(I) was precipitated once in diethyl ether and then taken for dialysis against methanol to remove the remaining IL(I) monomer. After 48 hours of dialysis, PIL(I) was collected by precipitation in diethyl ether and dried under vacuum (35 °C) till a constant weight was obtained with a final yield of 60%. All PIL(X) (X = Cl, Br, I) were analysed by ¹H NMR to confirm the absence of any residual monomer (Fig. S1). Macromolecular characteristics of the PILs were determined by size exclusion chromatography (SEC) (table S1). Prior to SEC analysis, all PILs were converted to PIL(NTf₂) by anion exchange to make them soluble in the mobile phase (THF) (SI, sec. 2a).

PIL(X)-stabilised RuNPs (Ru@PIL(X) NPs) (X = Cl, Br & I) were prepared using RuCl₃·xH₂O and RuBr₃·xH₂O as metal precursors and PIL(Cl), PIL(Br) or PIL(I) as stabilisers via polyol process. Different molar ratio between PIL(X) (repeating IL(X) units) to metal salt (*i.e.* 50:1, 10:1, 2:1) were used to synthesise Ru@PIL NPs.

Typically, 400 mg of PIL(X = Cl, Br & I) and required quantity of metal salt were dissolved in 40 ml ethylene glycol in a 200 ml Schlenk flask. After stirring for 4 hours at 750 rpm, the resulting dark yellow solution was degassed with argon and immersed in an oil bath pre-heated at 170 °C. The dark yellow solution slowly turned black, indicating the formation of Ru(0)NPs. Heating was continued for 1.5 hours to ensure complete conversion of ruthenium salt to Ru(0). Complete reduction of Ru(+2) salts and formation of NPs was confirmed by UV-vis spectroscopy analysis (see SI). Disappearance of the broad absorption band in the spectrum of the precursor after reduction indicates complete reduction of Ru(+2) into Ru(0). A representative example is given in Fig. S1 with the reduction of RuCl₃ in presence of PIL(Cl). PILs stabilised NPs were collected by centrifuging 5 ml of NP solution with 30 ml mixture of diethyl ether and acetone (50:50). After this initial centrifugation, RuNPs were dissolved in acetone (15 mL) and diethyl ether was added (20 mL); the resulting suspension was then subjected to centrifugation. This step was repeated once. The resulting sticky black product was next dissolved in 5 mL of methanol and centrifuged with 25 mL of diethyl ether. The resulting shiny black product was vacuum dried at 35 °C (0.8 mmHg) till a

constant weight was obtained (24 - 48h). This step ensures the removing of the different solvents, including ethylene glycol (b.p. = 197 °C). All centrifugations were carried out at 8000 rpm for 15 min at 15 °C. The resulting shiny black products **1Cl** (PIL(Cl)/Ru = 50), **2Cl** (PIL(Cl)/Ru = 10), **3Cl** (PIL(Cl)/Ru = 2), **2Br** (PIL(Br)/Ru = 10) and **2I** (PIL(I)/Ru = 10) were vacuum dried at 35 °C till a constant weight was obtained.

To obtain hydrophobic Ru@PIL(NTf₂) NPs, *i.e.* **2NTf₂**, a Br⁻ / NTf₂⁻ anion exchange was performed from **2Br**. In a typical anion exchange procedure, 10 ml aqueous solution of LiNTf₂ (4 molar equivalent) was added dropwise to 30 ml aqueous solution (1.5 mg/ml) of **2Br** under vigorous stirring, leading to the slow precipitation of **2NTf₂**. To ensure complete exchange, the mixture was stirred for 16 hours under ambient temperature. All operations were carried out under argon atmosphere. Resulting precipitates were washed several times with water and then dried under vacuum at 35 °C until a constant weight was obtained. The solubility of the different RuNPs was examined in a variety of solvents (Table S2). Alternatively, **2NTf₂** could be prepared from **2Cl**, following the same procedure. The reverse process, involving NTf₂⁻ / Br⁻ anion exchange, could also be performed on **2NTf₂**. In a typical procedure, excess of LiBr (4 molar equivalent) pre-dissolved in acetone was added dropwise to **2NTf₂** solution in acetone (1.5 mg/ml) and stirred overnight under inert atmosphere. Upon anion exchange, **2Br'** precipitated out of the solution. Removal of excess LiBr was accomplished by washing the precipitate with acetone. **2I** could also undergo a complete I⁻ / NTf₂⁻ anion exchange by using AgNTf₂ as the source of NTf₂⁻. Here, methanol was used as the solvent during anion exchange and AgI was obtained as the solid precipitate. AgI was removed by centrifugation to obtain a solution of **2NTf₂**, which was then evaporated under vacuum to obtain **2NTf₂** (SI, sec. 2c).

Characterizations of nanoparticles

Ru content of all NP samples was determined by thermo gravimetric analysis (TGA) using a TGA Q-500 from TA instruments. TGA was performed in two steps: in the first step, samples were heated till 600 °C under nitrogen to remove PILs. In the next step, air was introduced after 600 °C to facilitate removal of residual char by combustion. The residual weight obtained around 615 °C was considered as the Ru content as all carbon-based matter had been removed.

Particle sizes of RuNPs were determined by recording Transmission electron microscopic (TEM) image by Hitachi 7650 TEM operating at 80 kV in high-resolution mode. Samples for TEM analyses were prepared by putting a drop of NP solution (0.5 mg/ml in methanol) on a carbon coated copper grid and drying it for 90 minutes before analysis. Particle size and distribution were determined by measuring 200 particles at random locations by Image J software.

XRD patterns were recorded on a PANalytical X'pert MPD-PRO Bragg-Brentano θ - θ geometry diffractometer equipped with a secondary monochromator and an X'celerator detector over an angular range of $2\theta = 20$ -80°. The Cu-K α radiation was generated at 45 kV and 40 mA ($\lambda = 0.15418$ nm).

Particle size and ζ -potentials of NPs were determined by dynamic light scattering at 25 °C at a concentration of 0.5 mg/ml using Malvern Zetasizer ZS equipment. All the particle size analysis was carried out using methanol as the solvent. ζ -potentials were measured using folded capillary cells (DTS 1070). Based on the solubility, both water and methanol were used as solvent.

X-ray photoelectron spectroscopy (XPS) analysis was carried out in a K-Alpha X-ray Photoelectron Spectrometer from Thermo Fisher Scientific equipped with monochromatized AlK α source ($h\nu=1486.6$ eV). The full spectra (0–1350 eV) and high-resolution spectra were recorded with constant pass energy of 200 eV and 40 eV respectively. Ar⁺ sputtering was used for depth profiles and high-resolution spectra were processed with AVANTAGE software. All scans were corrected considering C(1s) as the reference (285.0 eV).

Hydrogenation procedure

Hydrogenation of unsaturated hydrocarbons was carried out in high pressure Parr reactor with internal volume of 45 ml and equipped with two valves, a manometer and a magnetic stirrer. In a typical hydrogenation, 5 ml of solvent were taken in a Schlenk to which 6 wt% of substrate and required quantity of NP catalyst were added. In the first method, solution of substrate and catalyst were charged into the reactor and the reactor was flushed three times with H₂ prior to sealing it with desired pressure. Then the reactor was immersed in the oil bath at the set temperature and reaction start time was noted when stirring speed reached 1000 rpm. Reaction was stopped by cooling the reactor by liquid nitrogen and releasing the H₂ pressure. In the second method of hydrogenation (preconditioning route), solution of substrate and catalyst was preheated to reaction temperature prior to flushing and sealing it with desired H₂ pressure. ¹H NMR analysis was used to determine conversion of substrate. In case of phenol hydrogenation, diethyl ether was used to extract the product and after evaporating diethyl ether at room temperature (15 min), product was analysed by ¹H NMR. When organic solvents were used as a solvent for hydrogenation, aliquots were diluted with deuterated solvents for ¹H NMR analysis.

Conversion and selectivity of some hydrogenation reactions were also determined by a Thermo Scientific GC-MS with Trace Ultra GC and Trace DSQ MS. Instrument was equipped with a RESTEK Rtx-5 Sil MS column (0.25 mm \times 30 m) and helium (0.8 ml/min) was used as the carrier gas.

Catalyst recycling

NP recycling for hydrogenation was carried out with 2Cl using phenol as a substrate. After 25 min. of hydrogenation, product was extracted with diethyl ether. Then, required quantity of phenol was added to the NP solution and reactor was closed and was flushed thrice with H₂ before sealing it at a desired pressure. Reactor was immersed in an oil bath at required temperature and start time was noted when stirring speed reached 1000 rpm. After completion of hydrogenation, the same procedure was repeated for the next cycle.

Conflicts of interest

There are no conflicts to declare.

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