Efficient Hydrogen Evolution from Dimethylamine Borane, Ammonia Borane and Sodium Borohydride Catalyzed by Ruthenium and Platinum Nanoparticles Stabilized by an Amine Modified Polymer Immobilized Ionic Liquid: a Comparative Study

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Abstract

Platinum and ruthenium nanoparticles stabilised by an amine modified polymer immobilised ionic liquid (MNP@NH$_2$-PEGPIILS, M = Pt, Ru) catalyse the hydrolytic liberation of hydrogen from dimethylamine borane (DMAB), ammonia borane (AB) and NaBH$_4$ under mild conditions. While RuNP@NH$_2$-PEGPIILS and PtNP@NH$_2$-PEGPIILS catalyse the hydrolytic evolution of hydrogen from NaBH$_4$ with comparable initial TOFs of 6,250 molesH$_2$.molcat^{-1}.h^{-1} and 5,900 molesH$_2$.molcat^{-1}.h^{-1}, respectively, based on the total metal content, RuNP@NH$_2$-PEGPIILS is a markedly more efficient catalyst for the dehydrogenation of DMAB and AB than its platinum counterpart, as RuNP@NH$_2$-PEGPIILS gave initial TOFs of 8,300 molesH$_2$.molcat^{-1}.h^{-1} and 21,200 molesH$_2$.molcat^{-1}.h^{-1}, respectively, compared with 3,050 molesH$_2$.molcat^{-1}.h^{-1} and 8,500 molesH$_2$.molcat^{-1}.h^{-1}, respectively, for PtNP@NH$_2$-PEGPIILS. Gratifyingly, for each substrate tested RuNP@NH$_2$-PEGPIILS and PtNP@NH$_2$-PEGPIILS were markedly more active than commercial 5wt % Ru/C and 5wt% Pt/C, respectively. The apparent activation energies of 55.7 kJ mol^{-1} and 27.9 kJ mol^{-1} for the catalytic hydrolysis of DMAB and AB, respectively, with RuNP@NH$_2$-PEGPIILS are significantly lower than the respective activation energies of 74.6 kJ mol^{-1} and 35.7 kJ mol^{-1} for its platinum counterpart, commensurate with the markedly higher initial rates obtained with the RuNPs. In comparison, the apparent activation energies of 44.1 kJ mol^{-1} and 46.5 kJ mol^{-1}, for the hydrolysis NaBH$_4$ reflect the similar initial TOFs obtained for both catalysts. The difference in apparent activation energies for the hydrolysis of DMAB compared with AB also reflect the higher rates of hydrolysis for the latter. Stability and reuse studies revealed that RuNP@NH$_2$-PEGPIILS recycled efficiently as high conversions for the hydrolysis of DMAB were maintained across five runs with the catalyst retaining 97% of its activity.

This article is dedicated to the memory of Professor Stephen A. Westcott, a great ambassador for chemistry in Canada and across the globe and the best and most sincere of friends.

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Graphical Abstract
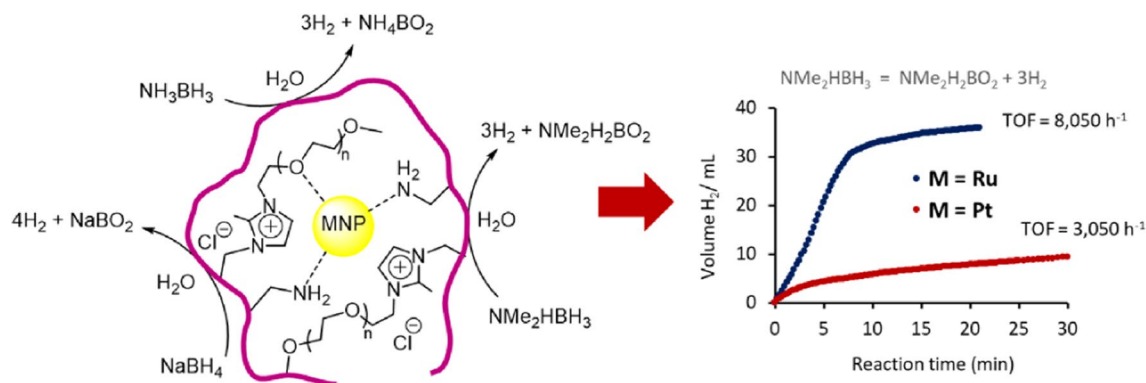
Keywords Ammonia borane · Dimethylamine borane · Catalytic dehydrogenation · Ruthenium and platinum nanoparticles · Kinetics and deuterium labelling

1 Introduction

The limited reserves of fossil fuels coupled with the negative environmental impact resulting from our continued reliance as a major source of energy is placing increasing pressure on developing an alternative clean and sustainable energy vector [1–4]. To this end, green hydrogen has attractive credentials as a clean and sustainable energy carrier for use in stationary and transport applications as it has a suitable gravimetric energy density (142 MJ kg^{-1} vs 54 MJ kg^{-1} for natural gas) and can be generated either from the electrolysis of water or from water splitting, generating oxygen as the only by-product [5–14]. However, the safe large-scale storage and transportation of such a highly flammable gas and its low volumetric energy density are major challenges that must be addressed if this technology is to become a practical reality and viable [15, 16]. One potential solution is to store the hydrogen either in the form of a low molecular weight solid or liquid hydride or to absorb it within the channels of a porous material [17–24]. In this regard, in addition to sodium borohydride [25–30], amine boranes have attracted significant interest as possible hydrogen storage materials because they are highly stable, have a high hydrogen content and are non-toxic and water soluble [31–39]. While ammonia borane (AB) has the highest hydrogen content (19.6 wt%), dimethylamine borane (DMAB) is *ca.* 30 times less expensive and as such considerable effort is currently being committed to developing cost effective catalysts for the facile and controlled liberation of hydrogen from this substrate [40–61].

The dehydrogenation of one mole of DMAB in organic media only liberates 1 mol of H$_2$ (Eq. 1) and while high rates of hydrogen production have been achieved with homogeneous catalysts under relatively mild conditions, they

suffer from poor long-term stability, often require expensive ligands and are difficult to recover after use [62–76]. Heterogeneous catalysts offer several advantages in terms of good thermal stability, range of operating temperatures, ease of recovery and integration into a device [77–82]. To the end, nanoparticle-based catalysts have attracted particular attention as their activity can be controlled through their size, and thereby surface area to volume ratio and number of active sites, as well as their morphology, however, the high surface area of metal NPs can lead to self-aggregation under the conditions of catalysis, forming larger species that are less active [83–93]. One approach with the potential to prevent aggregation has been to stabilize the nanoparticles by encapsulation into a suitable support such as a metal oxide or zeolite, a porous carbon material e.g. graphene oxide or reduced graphene oxide, polymers or porous organic cages and MOF [94]. To this end, there have been several recent examples of NPs that catalyse the dehydrogenation of DMAB with encouraging performance profiles either solventless or in organic media including mono-, bi and tri-metallic systems encapsulated in PVP [41, 42, 55, 56, 95, 96], graphene oxide and reduced graphene oxide [44–46, 58, 97–99], Vulcan carbon [49], ceria, alumina or titania [100–103], MOFs [104–109], hydrophilic polymers [110], and MW carbon nanotubes [111]. Moreover, it is becoming increasingly more evident that the encapsulation of NPs has additional benefits for catalysis; these include control of the growth and morphology due to confinement [112–117], dramatic enhancements in catalyst performance arising from strong metal support interactions [118–123], and significant improvements in activity and selectivity by incorporating surface functionality or organic modifiers/ligands to modulate the surface electronic structure and/or steric environment as well as the solubility of the reactants [124–127]. In

contrast to the dehydrogenation in organic media, the hydrolytic release of hydrogen from DMAB liberates three moles of H_2 (Eq. 2), however, there are surprisingly few reports of this hydrolysis catalysed by ruthenium nanoparticles and as such there is still a need to identify cost effective catalysts for the rapid and controlled hydrolysis of DMAB under mild conditions and to develop an understanding of the factors that influence catalyst efficacy.

While ionic liquids have also been used for the stabilisation of metal nanoparticles [128–130] and their applications in a broad range of fundamentally important transformations explored [131–134], there do not appear to be any reports of the use of ionic liquid stabilised NPs for the catalytic release of hydrogen from DMAB, which is somewhat surprising as amine boranes have been widely used as hydrogen donors for catalytic transfer hydrogenations [135–151]. This is even more surprising considering that ionic liquids promote the dehydrogenation of ammonia borane and as such might be expected to show a cooperative or synergistic effect with NPs [152–157]. Ionic liquids have also been grafted to supports such as polymers [158–167], mesoporous silica [168–171] and MOFs [172–179] to combine their favourable characteristics, such as the stabilization of nanoparticles through weak electrostatic interactions in the same manner as an IL, with covalent attachment to a support which would immobilise the ionic liquid, facilitate recovery of the catalyst and reduce the amount of ionic liquid as the catalyst would be confined within the support. Moreover, the tuneable physicochemical properties and modular synthesis of PIILs should enable the ionic environment, charge density and distribution to be modified, additional surface functionality to be introduced and the stoichiometry of the metal precursor to be controlled to facilitate the synthesis of synergetic bi- and multimetallic nanoparticles and thereby improve catalyst efficacy and develop new processes and technology to meet the criteria required for commercial applications. Although support-grafted ionic liquids are finding wide ranging applications for the stabilisation of NPs and molecular catalysts there are only a few reports of their use as supports to stabilise NPs for the hydrolytic release of hydrogen from storage materials. In the first of these, highly dispersed PdAuNPs stabilized by an imidazolium-modified porous organic polymer catalyses the hydrolytic release of H_2 from AB more efficiently than either of its monometallic counterparts [180], while RuNPs supported on a polymeric ionic liquid catalyses the synthesis of benzimidazole from CO_2 and 1,2-diamines by reductive dehydrogenation of DMAB as well as the DMAB-mediated reduction of olefins and nitroarenes [181, 182]. We have been developing heteroatom donor functionalised PIILs as supports for the stabilisation of NPs to determine whether the heteroatom donor can supplement the weak stabilisation provided by the ionic liquid fragment, influence the growth of the NPs or modify the surface electronic structure and

steric properties and thereby exploit the beneficial influence that ligands can impart on the performance of heterogeneous nanocatalysts [183–189]. To this end, we recently reported that platinum and ruthenium NPs stabilised by phosphine or amine-modified PIILs catalyse the hydrolytic dehydrogenation of $NaBH_4$ [190, 191]. In a subsequent study to explore the efficacy of amino-modified PIIL stabilised Pt and Ru nanoparticles as catalysts for the DMAB-mediated reduction of quinoline, we discovered that their disparate efficiency may be associated with the different rates of hydrogen evolution from the DMAB as this would influence the availability of surface hydride species [192]. We have now conducted a thorough and detailed comparison of the performance of amino-functionalised PEG-modified PIIL stabilised ruthenium and platinum NPs as catalysts for the hydrolytic dehydrogenation of DMAB, AB and $NaBH_4$ and herein report the results of this study. Surprisingly, RuNP@NH_2-PEG-PIILS is a markedly more active catalyst for the hydrolysis of DMAB and AB than its platinum counterpart whereas both catalysts gave comparable rates for the hydrolysis of $NaBH_4$. Moreover, the TOF of 8,300 h^{-1} for the aqueous phase dehydrogenation of DMAB using RuNPs stabilised by PEG-modified amine-decorated polymer immobilized ionic liquid is among the highest to be reported under mild conditions but lower than the 14,926 h^{-1} obtained with a PtRu nanocatalyst stabilised by Vulcan carbon; currently the most efficient state-of-the-art catalyst for the aqueous phase dehydrogenation of this substrate [49]. In addition, regardless of the catalyst, the hydrolytic dehydrogenation of ammonia borane was substantially faster than DMAB. Preliminary, kinetic studies with deuterium isotope effects were undertaken to probe the mechanism of hydrolysis and possible pathways are discussed.

$$NMe_2HBH_3 \xrightarrow{\text{toluene}} NMe_2BH_2 + H_2 \qquad (1)$$

$$NMe_2HBH_3 + 2H_2O \xrightarrow{\text{water}} \left[NMe_2H_2\right]\left[BO_2\right] + 3H_2 \qquad (2)$$

2 Results and Discussion

2.1 Synthesis and Characterisation of Precatalyst 1a and Nanoparticle Catalysts 2a-b

The composition of the tetrachloroplatinate loaded precursor [$PtCl_4$]@NH_2-PEGPIILS (**1a**) and the polymer immobilised ionic liquid stabilised platinum and ruthenium nanoparticles **2a-b** required for this study are summarised in Fig. 1. Precursor **1a** was prepared by impregnation of the corresponding polymer NH_2-PEGPIIL with the tetrachloroplatinate anion such that complete exchange of all the bromide and

Fig. 1 Composition of $[PtCl_4]^{2-}$ impregnated amine-decorated PIIL, PtCl$_4$@NH$_2$-PEGPIILS (**1a**) and the corresponding PIIL-stabilised platinum nanoparticles PtNP@NH$_2$-PEGPIILS (**2a**) and corresponding ruthenium nanoparticles RuNP@NH$_2$-PEGPIILS (**2b**)
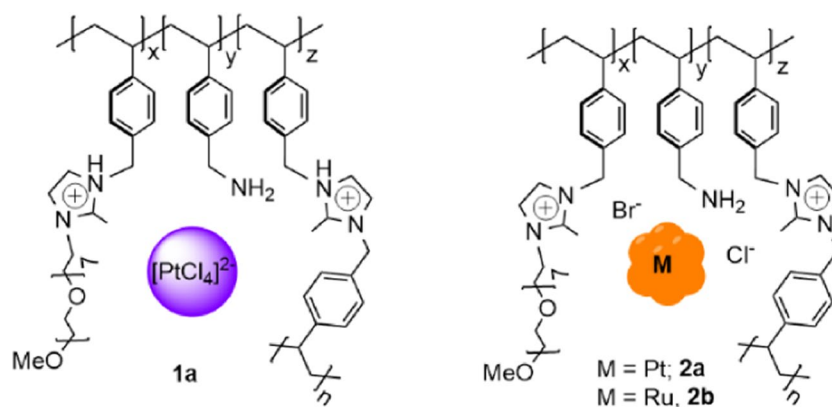
chloride would afford an amine to platinum ratio of one; the resulting precursor **1a** was isolated as a dark red solid in near quantitative yield. Quantitative analysis of the Cl 2p and Br 3d components of the XPS spectrum of **1a** revealed that the exchange was not complete as evidenced by the presence of both bromide and chloride, although as expected impregnation of NH$_2$-PEGPIIL with $[PtCl_4]^{2-}$ resulted in a significant reduction of the bromide content as evidenced by a comparison of the bromide to chloride ratio of 1:0.22 for NH$_2$-PEGPIIL and 1:1.75 for **1a**; this was supported by ICP OES analysis of the precursor which gave a bromide to chloride ratio of 1:2.2. The corresponding amine decorated polymer immobilised ionic liquid stabilised platinum nanoparticles PtNP@NH$_2$-PEGPIILS (**2a**) was obtained by sodium borohydride mediated reduction of **1a** in ethanol and isolated as a free-flowing black powder and its ruthenium counterpart **2b** was prepared as previously described [191]. The solid state ^{13}C NMR spectrum of **1a** contains a series of signals associated with the carbon atoms of the imidazolium ring and the aromatic carbons at δ 124 and δ 146 ppm, high field signals at δ 11–49 ppm for the methyl group on the imidazolium ring and the methylene units of the polymer backbone and the benzylamine as well as an intense signal at δ 71 ppm for the methylene units of the PEG and a weaker signal at δ 58 ppm for the terminal OMe. The solid-state ^{13}C NMR spectra of **2a-b** were identical that of the polymer support. Comparison of the solid state ^{15}N NMR spectrum for the polymer support, NH$_2$-PEGPIIL, with that for **1a** provided convincing evidence for a Pt–N interaction as the former contains three signals at δ -195/-207 and δ -332 ppm for the nitrogen atoms in the imidazolium ring and the amine, respectively, while the latter contains an additional signal at δ -291 ppm; the 41 ppm shift to low field is indicative of a platinum coordinated amine (Fig. S13 in the supporting information). The IR spectra of the polymer, NH$_2$-PEGPIIL, precatalyst **1a** and catalysts **2a-b** each contain bands at *ca*. 1580 cm^{-1} and 1605 cm^{-1} characteristic of C=C and C=N stretching vibrations of the imidazolium ring and a band at *ca*. 1450 cm^{-1} due to the C-N(imidazolium or amine)

stretching vibration confirming that the ionic liquid monomer was incorporated into the polymer. The thermal stability of the NH$_2$-PEGPIIL support was investigated by thermogravimetric analysis which showed an initial weight loss just below 100 °C associated with removal of a minor amount of physiosorbed ethanol and/or water; this was followed by three major degradation pathways between 260–650 °C, confirming its suitability as a support for the stabilisation of nanoparticles for use in catalysis. Moreover, the TGA profiles for **2a-b** revealed that these catalysts begin to decompose close to 210 °C, which is well below the temperatures typically required for the release of hydrogen from storage materials. The platinum and ruthenium loadings in **1a** and **2a-b** were determined using ICP-OES. In addition, since NH$_2$-PEGPIIL is a mixed bromide/chloride salt and **2a** and **2b** were generated by reduction of the corresponding metal chloride impregnated precursors, ICP-OES analysis was also undertaken to establish the chloride and bromide composition of **2a-b** as the amount and type of halide is likely to influence their efficacy. To this end, the chloride to bromide ratios of 6.25:1 and 7.0:1 in **2a** and **2b**, respectively, confirm that both contain similar amounts of residual bromide. This was supported by quantitative analysis of the Cl 2p and Br 3d components of **2a** and **2b** which was used to determine the relative amounts of chloride and bromide retained after reduction of the metal halide impregnated precursor; reassuringly, the ratios of 7.2:1 and 7.9:1 for **2a** and **2b**, respectively, support those determined by ICP-EOS.

Surface characterisation of the polymer, precatalyst **1a** and catalysts **2a-b** was undertaken by X-ray photoelectron spectroscopy (XPS). Due to the limitations associated with using advantageous carbon as the references [193], peak assignments were mainly based on the characteristic BE separations between the elements. The local nitrogen environment of the polymer was fitted to two peaks at 397.4 eV and 395.6 eV characteristic of nitrogen in an imidazolium ring and an amine, respectively (see Fig. S15 in the support information). The C 1 s region was also consistent with the polymer composition as it was fitted to three peaks, one at

280.6 eV for C–C/C-H species and two at 282.3 eV and 281.2 eV characteristic of C-O and C-N species, respectively [189]. The N 1 s region of the tetrachloroplatinate loaded precatalyst **1a** was also fitted to two major peaks at 397.4 eV and 395.6 eV corresponding to imidazolium and amine species, respectively (see Fig. S21 in the supporting information) [189]; both peaks do not appear to shift relative those in the polymer suggesting that the chemical environment is unchanged. An additional minor component was also fitted at 395.0 eV, which may be indicative of a Pt–-N interaction. The Pt 4f region of the tetrachloroplatinate-loaded precursor was fitted to two pairs of $4f_{7/2}$ and $4f_{5/2}$ spin orbit doublets, consistent with two Pt 4f electronic environments (Fig. 2a). The binding energies of the major $4f_{5/2}$ and $4f_{7/2}$ peaks at 71.5 eV and 68.2 eV correspond to Pt(II) coordinated to chloride as the Pt $4f_{5/2}$ and Cl $2p_{3/2}$ and Pt $4f_{7/2}$ and Cl $2p_{3/2}$ separation of 121.3 eV and 124.6 eV, respectively, are comparable to literature reported values for a Pt(II)-Cl species [194–199], while the minor $4f_{5/2}$ and $4f_{7/2}$ doublet at 72.8 eV and 69.5 eV is shifted to higher binding energy and most likely corresponds to platinum coordinated to amine, as the separation of 3.3 eV between these peaks and the difference on the BE scale of 326.7 eV between the $4f_{7/2}$ state and the N 1 s is comparable to values previously reported for a Pt–-N interaction [200–203]. Such a peak shift to higher binding energy indicates that the formation of a Pt–-N interaction renders the platinum more electron deficient, which may be a result of the lower negative charge at platinum due to substitution of a chloride in $[PtCl_4]^{2-}$ for a neutral amine. The peak with a binding energy centred at 64.2 eV corresponds to residual bromide, derived from the PEG-modified imidazolium monomer, and was fitted to two pairs of $3d_{5/2}$ and $3d_{3/2}$ doublets, which mostly likely correspond to bromide anion and Pt-coordinated bromide [197]. The Pt 4f region of the XPS spectrum of catalyst **2a** (Fig. 2b) was fitted to two pairs of $4f_{7/2}$ and $4f_{5/2}$ doublets and the separation between the BEs of the Pt $4f_{7/2}$ peaks and the O 1 s peak of 465.4 eV and 463.8 eV is consistent with Pt metal and PtO$_2$, respectively [204–206]. In the case of catalyst **2b**, the Ru 3p region was analysed due to overlap of the C 1 s and Ru 3d regions and the broad peak at 459.5 eV was fitted to two Ru $3p_{3/2}$ peaks; the peak at

higher BE was assigned to RuO$_2$ while the one at lower BE was attributed to Ru(0) (Fig. 2c). This assignment was based on the separation between these peaks and the aliphatic C 1 s peak as the values of 177.7 eV and 180.2 eV for this difference are consistent with previously reported values for metallic ruthenium and RuO$_2$, respectively [207–211]. The peaks assigned to RuO$_2$ species are probably due to surface oxidation of the preformed ruthenium nanoparticles. Finally, while Na and B 1 s peaks in the XPS spectra for **2a** and **2b** confirmed the presence of a borate salt such as NaBO$_2$ or NaB(OH)$_4$ these were subsequently removed by extraction with water. The powder XRD pattern for **2b** contained diffraction peaks at 2θ = 28.1°, 35.2°, 40.3°, 54.5°, 58.1°, 59.6°, 65.8°, 67.2°, 69.8° and 74.3° which index to the (110), (101), (200), (210), (211), (220), (002), (310), (112), (301) and (202) lattice planes of the tetragonal phase of RuO$_2$ with the P42/mmm space group (ICDD No. 00–040-1290), consistent with the reported literature. The absence of diffraction peaks for metallic ruthenium suggest that the nanoparticles are highly dispersed with sizes < 2.5 nm, which was supported by TEM analysis. Similarly, the powder XRD pattern for **2a** contained characteristic diffraction peaks at 2θ = 27.9°, 34.7°, 34.8°, 39.6°, 40.2°, 40.3°, 53.8°, 57.7°, 58.8°, 65.0°, 65.6° which index to (110), (011), (101), (020), (200), (111), (121), (220), (002), (130), (221) lattice planes for the orthorhombic phase of β-PtO$_2$ (ICDD No. 01–073-2361) and the absence of diffraction peaks associated with metallic PtNPs is also consistent with their small size and high dispersion, as described below. TEM micrographs of **2a** and **2b** showed that the platinum and ruthenium nanoparticles were ultrafine and near monodisperse with average diameters of 1.70 ± 0.5 nm and 2.46 ± 0.4 nm, respectively; illustrative micrographs and the corresponding distribution histograms resulting from sizing of > 100 particles are shown in Fig. 3 a-f.

2.2 PtNP and RuNP Catalysed Hydrogen Evolution from Dimethylamine Borane, Ammonia Borane and NaBH$_4$

Having recently reported that PtNPs and RuNPs stabilised by heteroatom donor decorated polymer immobilised ionic

Fig. 2 Pt 4f core level XPS spectra of (**a**) **1a** and (**b**) **2a** and (**c**) Ru 3p XPS spectrum of **2b**
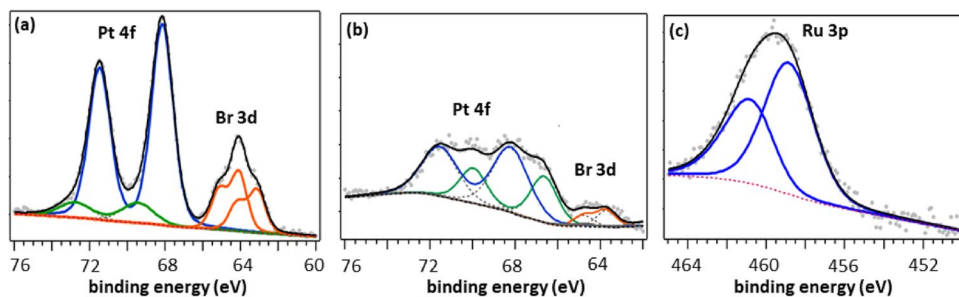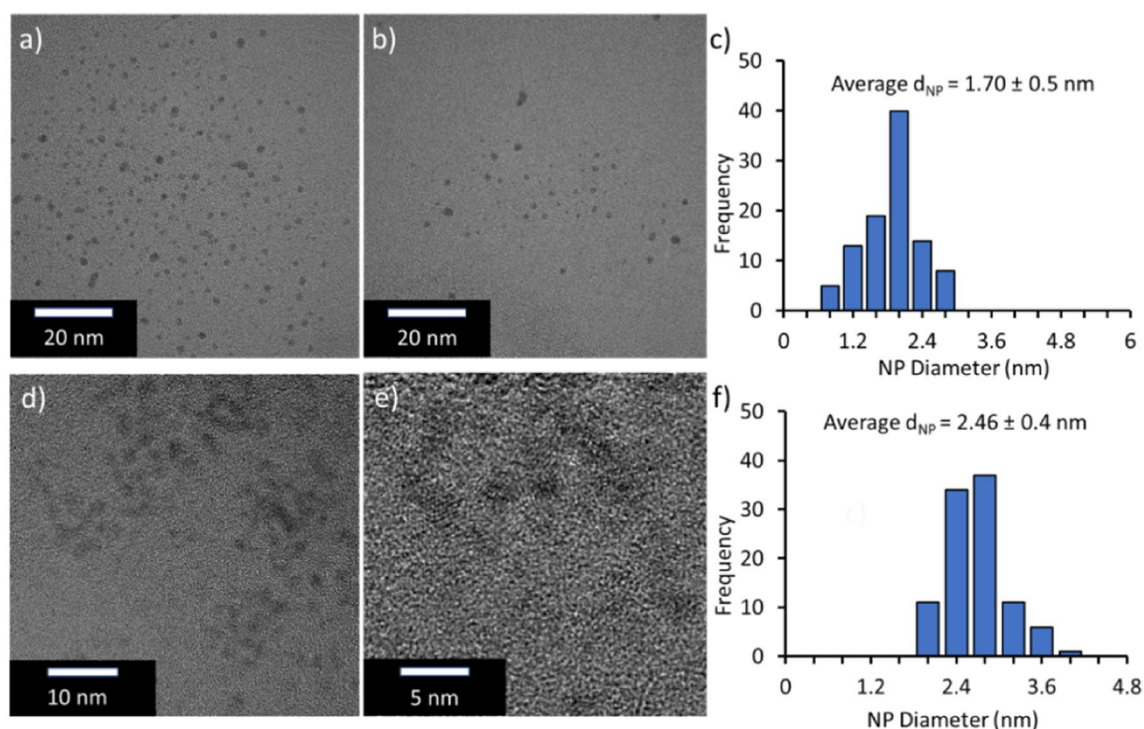
Fig. 3 TEM images and corresponding sizing histograms of (**a-c**) PtNPs for **2a** and (**d-f**) RuNPs for **2b** determined by counting > 100 particles

liquids are efficient catalysts for the hydrolytic evolution of hydrogen from sodium borohydride, this project was extended to compare the catalytic efficacy of amino-decorated PIIL-stabilized Pt and Ru nanoparticles for the hydrolysis of DMAB, an inexpensive model substrate for ammonia borane, and discovered that RuNP@NH$_2$PEGPIILS (**2b**) was a markedly more efficient catalyst than its platinum counterpart **2a**. Preliminary testing was conducted using 0.25 mol% of **2a**-**b** to catalyse the hydrolytic liberation of hydrogen from 0.27 M DMAB at 313 K (Fig. 4a). Reactions were monitored by measuring the amount of hydrogen liberated with time by displacement of water from an inverted burette; the data was subsequently corrected by accounting for the background volume of hydrogen liberated under the same conditions at the same time in the absence of catalyst. The data in Fig. 4a shows that RuNP@NH$_2$-PEGPIILS (**2b**) is a markedly more efficient catalyst for the hydrolysis of DMAB

than its platinum counterpart (**2a**) as the former reached *ca.* 99% completion after 20 min with an initial total turnover frequency (TOF) of 8,300 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1}, whereas the latter only reached 22% conversion after the same time and 38% conversion when the reaction time was extended to 60 min, with an initial total TOF of 3,050 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1}. This difference in efficiency between **2a** and **2b** is even more evident when the initial TOFs are determined based on the estimated surface metal atoms (Table 1). For comparison, a catalytic hydrolysis conducted with 0.25 mol% Ru/C (5 wt%) only achieved 46% conversion after 20 min with an initial TOF of 2,800 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1} while 0.25 mol% Pt/C (5 wt%) only reached 24% conversion after 35 min with an initial TOF of 2,200 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1} (Fig. S1 in the supporting information). Moreover, pre-stirring the Ru/C and Pt/C with a homogeneous solution of NH$_2$-PEGPIIL in water for 12 h prior to performing the hydrolysis only

Fig. 4 Hydrolytic liberation of hydrogen from a 0.27 M solution of (**a**) dimethylamine borane (**b**) ammonia borane and (**c**) NaBH$_4$ as a function of time at 313 K catalysed by 0.25 mol% **2a** and **2b**
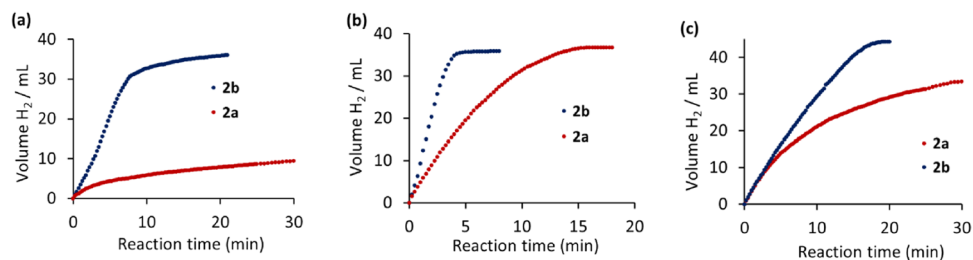
Table 1 Summary of the initial turn over frequencies and conversions for the hydrolysis of 0.27 M DMAB, AB and NaBH$_4$ catalysed by **2a**, **2b**, Pt/C and Ru/C at 313 K.[a]

| Substrate | Initial total TOF[b] and (TOF)[c] Conversion (%)[d] | | | |
	2a	Pt/C	2b	Ru/C
DMAB	3,050 (7,625)	2,200	8,300 (29,122)	2,800
	38% (60 min)	24% (35 min)	100% (20 min)	46% (20 min)
AB	8,500 (21,250)	5,700	21,200 (74,200)	7,750
	99% (15 min)	93% (11 min)	98% (5 min)	93% (7 min)
NaBH$_4$	5,900 (14,750)	5,050	6,250 (21,875)	5,400
	68% (30 min)	45% (20 min)	92% (18 min)	67% (18 min)

[a] *Reaction conditions*: 2.0 mL of 0.27 M substrate, temp = 313 K, 0.25 mol% **2a**, **2b**, Pd/C, Ru/C. [b] Total turnover frequency in mole$_{H2}$.molcat^{-1}. h^{-1} based on total metal loading and determined at *ca*. 20% conversion. [c] Turnover frequency in mole$_{H2}$.molcat^{-1}.h^{-1} based on the estimated surface metal atoms; full details of this calculation are provided on pages S12 and S13 of the supporting information. [d] % Conversion determined at the time given in the parentheses

resulted in a marginal improvement in the initial TOF to 3,050 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1} and 2,300 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1}, respectively. A reference hydrolysis conducted by replacing the catalyst with 0.25 mol% NH$_2$PEG-PIIL confirmed that the metal nanoparticles were necessary for catalysis.

Having established that **2a-b** catalyse the hydrolysis of DMAB, the same protocol was applied to the hydrolysis of 0.27 M ammonia borane (AB) to assess their relative efficacy and compare their performance as a function of the substrate. Under the same conditions, **2b** was also significantly more active than **2a**, as measured by the volume of hydrogen released at the onset of the reaction, and the initial total TOFs of 21,200 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1} and 8,500 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1}, respectively, and the relative difference in these TOFs as measured by their ratio, is comparable to that for the hydrolysis of DMAB (Table 1). Moreover, the initial rates of hydrolysis of AB for catalysts **2a** and **2b** are considerably faster than those for the hydrolysis of DMAB and near complete conversions were obtained in much shorter reaction times (Table 1). Reassuringly, **2a** and **2b** are both markedly more active as catalysts for the hydrolytic dehydrogenation of AB than commercially available 5 wt% Ru/C and Pt/C, which both reached 93% conversion, with initial TOFs of 7,750 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1} and 5,700 mole$_{H2}$.mol$_{Pt}$$^{-1}$. h^{-1}, respectively; the higher activity obtained with Ru/C is in keeping with its efficacy for the hydrolysis of DMAB described above. A review of the literature revealed that initial TOFs for the PtNP-catalysed hydrolysis of AB have been reported from 1,962 h^{-1} up to 28,800 h^{-1} whereas those for RuNP based catalysts range from 2,400 h^{-1} to 43,000 h^{-1}; gratifyingly, **2a** and **2b** clearly compete with the more active of these. Although a comparison of the relative rates of hydrolysis of DMAB and AB described here with those reported in the literature should be treated with a degree of caution, this survey revealed the same trend in rates in that the hydrolysis of AB is typically much faster than DMAB

with both ruthenium and platinum nanoparticles [97, 105, 212–239]. However, while there do not appear to be any direct comparisons between the efficacy of platinum and ruthenium nanoparticles stabilised or confined on the same support, ruthenium nanoparticle-based catalysts appear to give higher initial rates than platinum nanoparticles.

Finally, as NaBH$_4$ is also a promising hydrogen storage material, the efficacy of **2a** and **2b** as catalysts for the hydrolytic liberation of hydrogen from aqueous 0.27 M sodium borohydride was examined. In stark contrast to DMAB and AB, the initial total TOFs of 5,900 mole$_{H2}$.mol$_{Ru}$$^{-1}$. h^{-1} and 6,250 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1} for the hydrolysis of NaBH$_4$, catalysed by **2a** and **2b**, respectively, are comparable to each other and any difference in catalyst efficacy only manifested itself in the final conversions which reached 92% for **2b** and 68% for **2a**. The corresponding comparison for the hydrolysis of NaBH$_4$ catalysed by 0.25 mol% Pt/C and Ru/C is consistent with the performance of **2a** and **2b** as reactions reached 45% and 67% conversion, respectively, and the initial total TOFs of 5,050 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1} and 5,400 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1}, respectively, were comparable to each other. In addition, these initial rates are only slightly lower than those obtained with the same catalyst loading of **2a** and **2b**; whereas, in contrast, **2a** and **2b** were distinctly more active as catalysts for the hydrolytic dehydrogenation of DMAB and AB than their Ru/C and Pt/C counterparts.

While evaluation of the efficiency of **2a**-**b** as catalysts for the hydrolysis of DMAB against literature reports of other ruthenium nanoparticle-based systems may have limited credibility or value due the disparate protocols and conditions, a review of the most recent literature revealed that **2b** appears to be among the most active ruthenium nanoparticle-based catalysts for the aqueous phase dehydrogenation of DMAB. For example, the initial TOF of 8,300 h^{-1} is a considerable improvement on 896 h^{-1}, 403 h^{-1} 362 h^{-1}, obtained with RuNPs stabilised by a PVP-graphene hybrd

support, PVP and GO, respectively [240], 812 h^{-1} with ceria supported RuNPs [52], 51 h^{-1} and 56 h^{-1} for Ru(acac)$_3$ derived nanoclusters generated in the presence of Al$_2$O$_3$ and PVP, respectively [56], 282 h^{-1} with a graphite-supported ruthenium nanocatalyst [241], 59 h^{-1} for RuNPs stabilized by confinement in the metal organic framework ZIF-8 [109], 173 h^{-1} for starch stabilised RuNPs [242], and 46 h^{-1} for the solventless dehydrogenation of DMAB with RuNPs loaded on cellulose [54], as well as a host of bi- and tri-metallic nanoparticles stabilised by reduced graphene oxide [45], PVP [41, 42, 95, 96], multi-walled carbon nanotubes [111], graphene oxide [58, 97–99, 243], polymer hydrogels [244], and silica [50]. While it is also slightly greater than the 7,500 h^{-1} obtained with PtNPs immobilised onto Ni(OH)$_2$ colloid [40] it is significantly lower than 14,926 h^{-1} for platinum-ruthenium nanoparticles decorated on Vulcan carbon, which is currently the most efficient supported nanoparticle catalyst for the hydrolytic evolution of hydrogen from DMAB [49]. To the best of our knowledge, the initial TOF of 8,300 h^{-1} obtained with **2b** is the highest to be reported for the aqueous phase hydrolytic dehydrogenation of DMAB catalysed by a monometallic RuNP-based catalyst, which may be due to a combination of the small size of the nanoparticles and the hydrophilic environment created by the PEGylated support which would affect dispersion of the catalyst in the aqueous phase as well as facilitate formation of the surface-coordinated hydrogen bonded array [NMe$_2$HBH$_2$-H–-H-OH] responsible for activation of one

of the H-OH bonds in water. While there are relatively few literature reports of the hydrolysis of DMAB using PtNP based catalysts, the total TOF of 3,050 h^{-1} obtained with **2a** is markedly higher than 49.2 h^{-1} with PtNPs decorated with a polyaniline-reduced graphene oxide composite [97] and 59 h^{-1} with platinum supported on Vulcan carbon [49] but lower than that of 4,151 h^{-1} obtained with Pt/C alloyed with nickel and 7,500 h^{-1} for PtNPs immobilised onto Ni(OH)$_2$ colloid [40].

The disparate performance of **2a** and **2b** as catalysts for the hydrolysis of DMAB and AB compared with their comparable performance for the hydrolysis of NaBH$_4$ prompted us to conduct a comparison of the kinetics on each of the reactions to investigate the rates as a function of temperature to determine the activation energies and to explore the effect of the catalyst and the DMAB/AB/NaBH$_4$ concentration on the rate of the hydrolysis. A series of hydrolytic reactions were performed over a range of temperatures between 294 and 318 K and the initial rate of hydrogen evolution monitored as a function of time. The apparent activation energies (E$_a$) for the hydrolysis of 0.27 M DMAB using a 0.25 mol% loading of **2a** and **2b** were calculated to be 74.6 kJ mol^{-1} and 55.7 kJ mol^{-1}, respectively, from the Arrhenius plot of ln(k) against 1/T shown in Fig. 5c-d; the initial rates were obtained from the linear region of the graphs in Fig. 5a-b. Such disparate activation energies are entirely consistent with the relative catalytic efficacy of **2a** and **2b**, as measured by the initial TOFs of 3050 mole$_{H2}$.mol$_{Pt}^{-1}$.h^{-1} and

Fig. 5 **a** Plots of volume of hydrogen liberated against reaction time for the hydrolysis of 2 mL of 0.27 M DMAB across a range of temperatures catalysed by (**a**) 0.25 mol% **2a** and (**b**) 0.25 mol% **2b** and the corresponding Arrhenius plots for the hydrolysis of DMAB catalysed by (**c**) **2a** and (**d**) **2b**; the initial rates (k) were calculated from the slopes of the fitted lines. Each hydrolysis was conducted in triplicate. Initial rate (k) = molH$_2$.min^{-1}
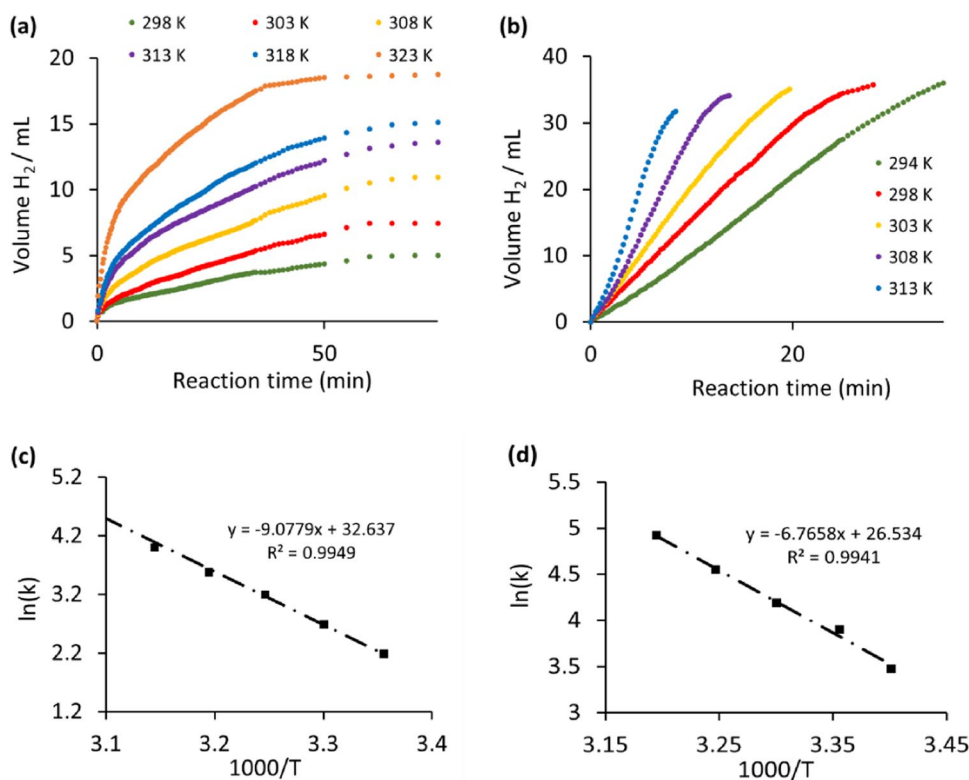
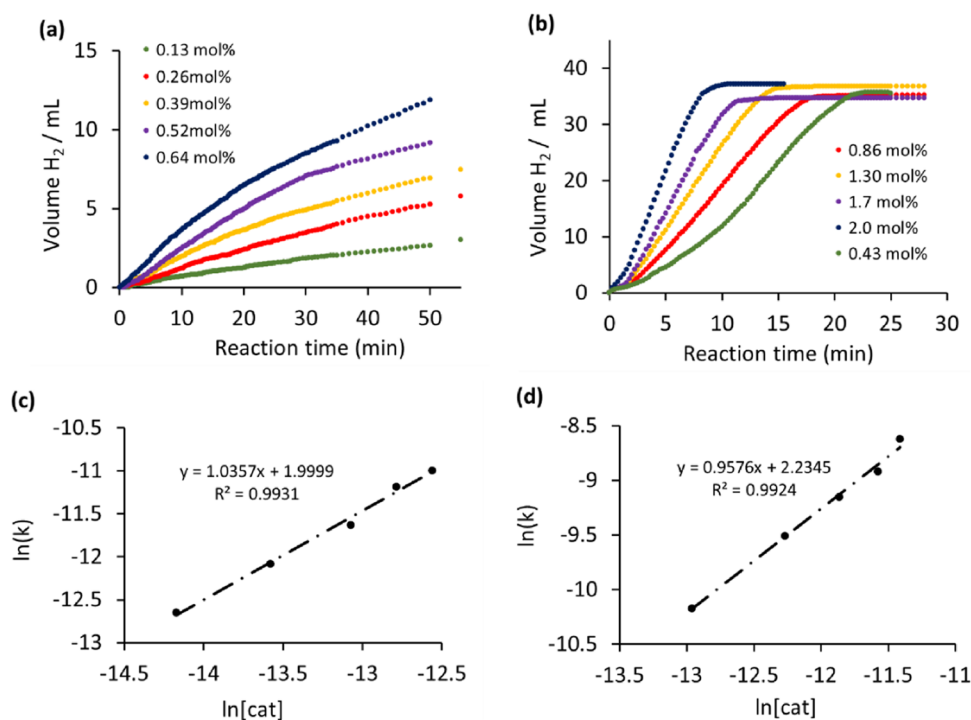8,300 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1}, respectively (vide supra). The corresponding activation energies for the hydrolysis of aqueous 0.27 M ammonia borane under otherwise identical conditions and across a similar range of temperatures, were determined to be 35.7 kJ mol^{-1} and 27.9 kJ mol^{-1} for 2a and 2b, respectively; these values are substantially lower than those for the hydrolysis of DMAB and reflect the higher rates of hydrolysis of AB under similar conditions. For comparison, the apparent activation energies of 44.1 kJ mol^{-1} and 46.5 kJ mol^{-1} for the hydrolysis of 0.27 M sodium borohydride catalysed by 2a and 2b, respectively, are similar and consistent with their comparable initial TOFs of 6,200 mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1} and 5,900 mole$_{H2}$.mol$_{Pt}$$^{-1}$.h^{-1}, respectively. The Arrhenius plots and the graphs showing the volume of hydrogen against time associated with the hydrolytic dehydrogenation of AB and NaBH$_4$ are available in the supporting information (Figs. S2-S3).

The hydrolytic dehydrogenation of DMAB was further explored by investigating the activity as a function of the concentration of 2a and 2b across various catalyst concentrations in 0.27 M DMAB. The logarithmic plot of the initial hydrogen generation rate against the catalyst loading were straight lines with slopes of 1.04 for 2a and 0.96 for 2b, confirming that the hydrolysis of DMAB is first order with respect to both catalysts (Fig. 6c-d). Similarly, kinetic studies for the hydrolysis of AB conducted with different concentrations of 2a and 2b were consistent with first order kinetics as evidenced from the slopes of 0.98 and 0.91, respectively, for the plot of the hydrogen generation rate against the catalyst concentration on the logarithmic scale
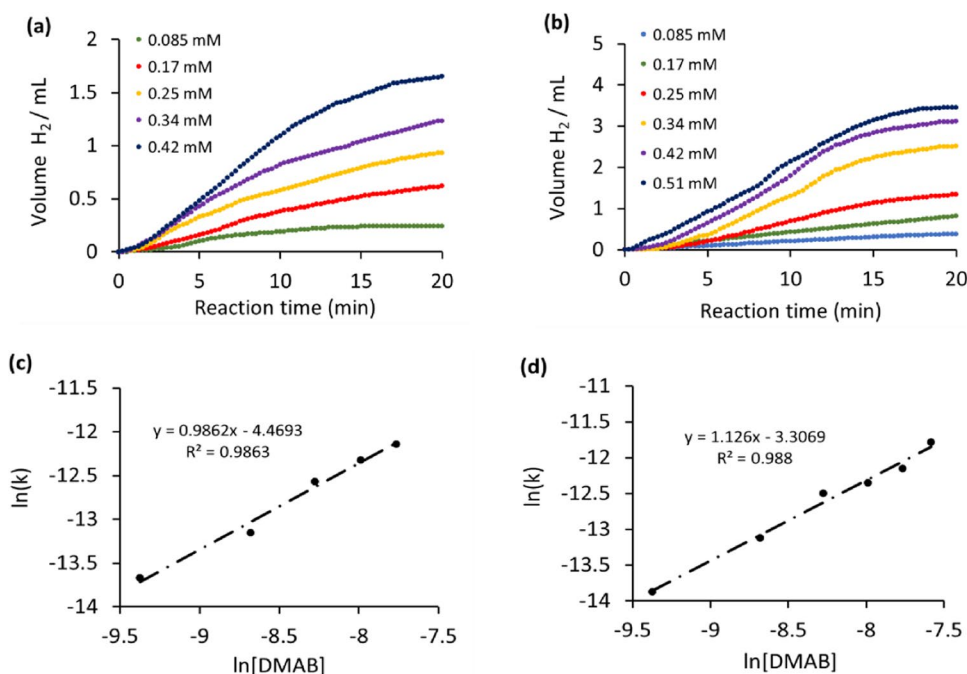
(Fig. S4). A review of the recent literature revealed that this data is in line with related reports of noble metal nanoparticle catalysed hydrolysis of DMAB and AB including slopes of 1.08 for ceria supported RuNPs [52], 1.03 for RuNPs loaded on cellulose [54], 0.86 for RuNP stabilised by a graphene oxide-PVP hybrid support [240], 1.01 for RuCu alloy NPs immobilised on reduced graphene oxide [45], 0.98 for RuPd@GO and 1.04 for RuNiPd nanoclusters immobilised on horse chestnut seed [51]. The corresponding study for the hydrolysis of a 0.27 M solution of sodium borohydride as a function of the concentration of 2a and 2b also gave straight line plots for the logarithm of the initial hydrogen generation rate against catalyst loading with slopes of 1.07 and 0.99, respectively, again these slopes indicate first order kinetics; details of which are available in Figures S4-S5 of the supporting information.

A study of the effect of the initial substrate concentration on the rate of hydrolysis of DMAB was also performed with 17 μmol of 2a and 2b and changing the initial concentration of DMAB ([DMAB]$_0$ = 0.085 mM to 0.51 mM) to obtain comparative kinetic data across catalyst/substrate ratios between 1:1 and 1:5 (Fig. 7); such low catalyst to substrate mole ratios were used to avoid saturation of the surface active sites, which would otherwise give zero order kinetics. The plot of the volume of hydrogen generated against time for each substrate concentration (Fig. 7a-b) was used to determine the initial rates. The corresponding logarithmic plots of the hydrogen generation rate against DMAB concentration gave slopes of 0.99 and 1.12 for 2a and 2b, respectively, confirming that the hydrolysis is first order

Fig. 6 a and (b) Volume of hydrogen generated as a function of time for the hydrolytic dehydrogenation of 2 mL of aqueous 0.27 M DMAB at 303 K catalysed by various concentrations of 2a and 2b, respectively; c and (d) plots of initial hydrogen generation rate versus logarithm of the catalyst loading for 2a and 2b, respectively. The initial rates (k) were determined from the slopes of the fitted lines. Each hydrolysis was conducted in triplicate. Initial rate (k) = molH$_2$.min^{-1}

Fig. 7 **a-b** Plots of volume of hydrogen liberated against time for the hydrolytic dehydrogenation of DMAB at 303 K catalysed by **2a** and **2b** (17 μmol) in water (200 mL), initial concentrations of DMAB ([DMAB]$_0$ = 0.085, 0.17, 0.25, 0.34, 0.42, 0.51 mM); **c-d** plots of the hydrogen generation rate against initial concentration of DMAB in logarithmic scale. The initial rates (k) were determined from the slopes of the fitted lines. Each hydrolysis was conducted in triplicate. Initial rate (k) = molH$_2$.min^{-1}

in substrate and that activation of DMAB is integral to the rate limiting step (Fig. 7c-d). Similar first order kinetics for the hydrolysis of DMAB or ethylenediamine bisborane have been reported for RuNPs supported on graphene oxide [58], cellulose [54], 2-hydroxyethyl starch-p-(2-acrylamide-2-methyl-1-propanesulfonic acid) hydrogel network [61], monodisperse graphite [241], a graphene oxide PVP hybrid [240], and oleylamine [245], as well as PtRu nanocatalysts supported on Vulcan carbon [49], graphene oxide stabilised PdCoNPs [44], monodispersed palladium-ruthenium alloy nanoparticles assembled on PVP [42], silica-based gold-nickel nanohybrid [50], a MOF decorated with monodisperse palladium-cobalt nanohybrids [104] and RuCu nanomaterials on reduced graphene oxide [45]. The corresponding study on the kinetics of hydrolysis of AB as a function of the substrate concentration also gave straight line plots for the logarithm of the initial hydrogen generation rate versus the concentration of AB with slopes of 1.08 and 1.03 for **2a** and **2b**, respectively; consistent with activation of AB in the rate limiting step (Fig. S6 in the supporting information). However, interestingly, while there have been reports of first order kinetics for the hydrolysis AB [232], the majority of studies appear to report that the rate of hydrolysis of AB does not depend on the substrate concentration, *i.e.* activation of AB is not involved in the rate determining step; in such cases the rate limiting step has been proposed to involve activation of an O–H bond of water, which may well be facilitated by a hydrogen bonding interaction between a hydrogen atom of water and either a hydridic B-H bond of a surface coordinated AB [246–249] or a hydridic NP-H [250, 251]. Under the same conditions, the corresponding kinetic studies for

the hydrolytic dehydrogenation of NaBH$_4$ using 26 μmol of catalysts **2a** and **2b** and changing the initial concentration of NaBH$_4$ to afford catalyst:substrate ratios ranging from 1:1 to 1:6 gave slopes of 1.01 and 0.97 for **2a** and **2b**, respectively, for the logarithmic plot of the initial hydrogen generation rate versus concentration of NaBH$_4$, meaning that this hydrolysis is also first order in NaBH$_4$; complete details are available in Figure S7 of the supporting information.

Kinetic isotope effect studies have proven to be an informative tool for elucidating information about the key rate limiting step (RLS) of the nanoparticle catalysed hydrolytic liberation of hydrogen from ammonia borane and sodium borohydride. While several mechanistic scenarios have been proposed for the hydrolysis of ammonia boranes including (1) rate limiting formation of an activated surface coordinated ammonia borane followed by attack of water to cleave the B-N bond and hydrolysis of the BH$_3$ [252], (2) formation of BH$_3$OHNH$_4$ by attack of water held proximal to a surface coordinated AB [253], and (3) dissociation of the B-N bond by attack of water at an activated surface bound ammonia borane followed by release of H$_2$ through attack of water on a transient hydridic NP-H, in much the same manner as the metal catalysed hydrolysis of NaBH$_4$ [254], and (4) rate limiting activation of one of the O–H bonds of water in a hydrogen-bonded array involving a hydridic B-H bond of a surface-coordinated ammonia borane and a water proton [246–248], it is clear that ammonia borane and NaBH$_4$ both act as sources of hydride and provide one hydrogen atom to the derived hydrogen while water provides the other in the form of a proton.
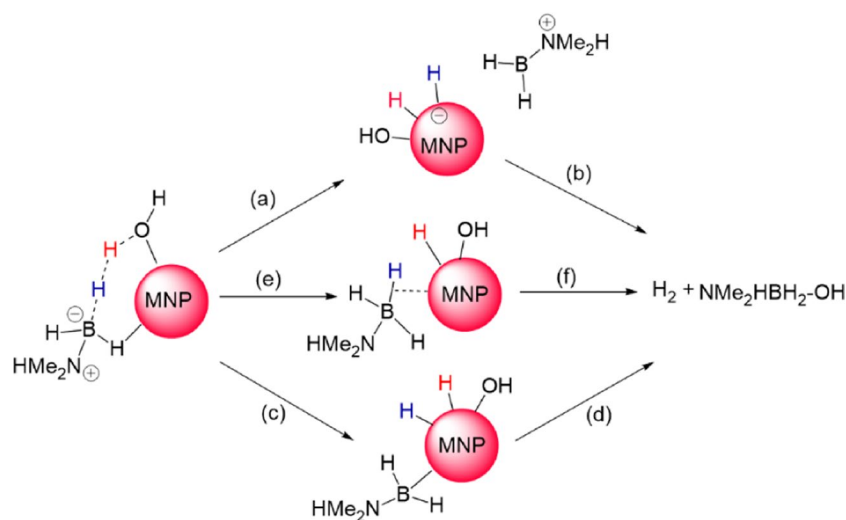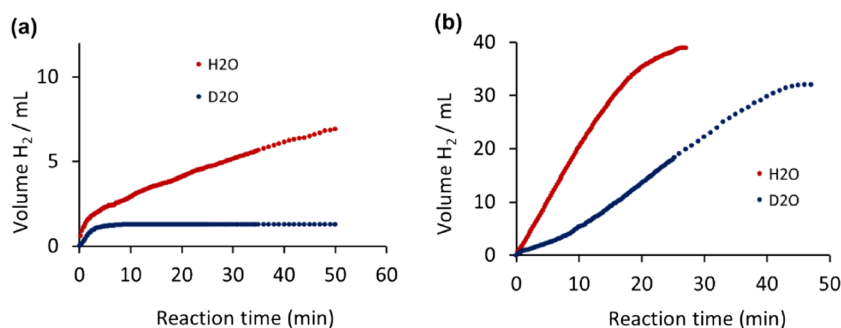
The role of water in the hydrolysis of DMAB catalysed by **2a** and **2b** was investigated by performing reactions in H$_2$O

and D_2O and monitoring the amount of hydrogen liberated with time to compare the initial rates and thereby determine the KIE. Reactions were conducted under the same conditions described above using 0.25 mol% **2a** and **2b** to catalyse the hydrolysis of 0.27 M DMAB at 303 K. A comparison of the initial rates of hydrolysis of DMAB in H_2O and D_2O catalysed by **2a** and **2b** showed that reactions were faster in H_2O than in D_2O with primary kinetic isotope effects (k_H/k_D) of 2.5 and 3.8, respectively (Fig. 8a-b); similar values of k_H/k_D were also obtained for the catalytic hydrolysis of a 0.27 M solution of AB in H_2O and D_2O using 0.25 mol% **2a** ($k_H/k_D = 2.6$) and **2b** ($k_H/k_D = 4.0$) and the associated data is presented in Figure S8a-b while that for the hydrolysis of 0.27 M $NaBH_4$ in H_2O and D_2O is presented in Figure S9a-b. These values for the KIE are comparable to that of 4.95 reported for the $Ni_2Pt@ZIF-8$ catalysed hydrolysis of ammonia borane [255] as well as atomically disperse platinum on the surface of Ni particles ($k_H/k_D = 4.0$) [224], CoNPs

supported on a covalent triazene framework ($k_H/k_D = 2.8$) [256], ultrasmall Pt nanoclusters on heterostructured NiO/Ni ($k_H/k_D = 2.8$) [257], CoPt nanocatalysts encapsulated in click dendrimer ($k_H/k_D = 2.46$) [249] and graphene oxide supported RhNPs ($k_H/k_D = 2.6$) [258] and is consistent with a mechanism involving rate limiting activation of one of the O–H (or O–D) bonds in water, which is activated/weakened by hydrogen bonding to one of the hydridic hydrogen atoms in DMAB.

While these KIE values are consistent with previously reported mechanisms in which a surface-coordinated hydrogen bonded array of the type Me_2NH-BH_2-H——H—OH, involving a hydridic B-H hydrogen and a proton on water, activates the O–H bond toward oxidative addition to generate a water derived M-H and a surface-coordinated DMAB, as shown in Fig. 9, it does not distinguish between oxidative addition of an O–H bond coupled with concerted hydride transfer from the DMAB (Fig. 9 path a) and a

Fig. 8 Hydrogen evolution from 2 mL of a 0.27 M solution of DMAB in H_2O (red) and D_2O (blue) at 303 K catalysed by 0.25 mol% (**a**) **2a** and (**b**) **2b**

Fig. 9 Proposed pathways for the metal nanoparticle catalysed hydrolytic evolution of hydrogen from the hydrogen bonded array Me_2NH-BH_2-H——H—OH via; **a-b** rate limiting oxidative addition of an O–H bond and hydride transfer followed by reductive elimination of H_2 and abstraction of a 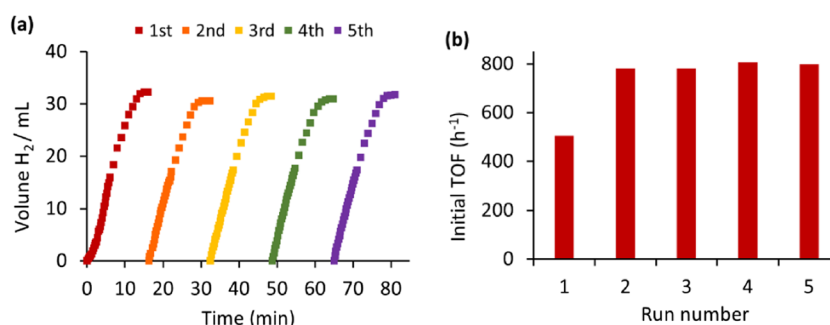surface hydroxide (**c-d**) double oxida-tive addition involving O–H and B-H bonds and subsequent reductive elimination of H_2 and [$HO-BH_2NMe_2H$] and (**e–f**) activation of an O–H bond followed by a σ-bond metathesis type process between the water derived M-H and the weakly σ-coordinated B-H of a DMAB

double oxidative addition of O–H and B-H bonds (Fig. 9 path c). The former pathway would liberate the hydrogen via reductive elimination of a water derived M-H and a DMAB derived M-H and generate NMe_2HBH_2-OH as an intermediate via electrophilic abstraction of a surface coordinated M-OH by the $[NMe_2HBH_2]^+$ cation (Fig. 9 path b), while the latter pathway would liberate the hydrogen and Me_2HBH_2-OH via reductive elimination (Fig. 9 path d). The remaining two B-H bonds in the monohydroxylated boron intermediate would subsequently activate in a similar manner to ultimately afford $[NMe_2H]_2[BO_2]$. While the above pathways are initiated by rate limiting oxidative addition of an O–H bond of water in a cooperative surface-coordinated hydrogen bonded array, we cannot unambiguously exclude the possibility that an O–H bond could be activated by hydrogen bonding between a surface adsorbed water and a DMAB-derived transient metal hydride, as described by Jagidar for the copper and Cu@Cu$_2$O core shell nanoparticle catalysed hydrolysis of sodium borohydride [254] and Guella for the palladium catalysed hydrolysis of NaBH$_4$ [259]. Alternatively, the hydrogen may be liberated via rate limiting activation of an O–H bond in water followed by a concerted σ-bond metathesis-type process between the resulting water-derived M-H and the σ-bonded B-H of a surface-coordinated DMAB (Fig. 9 path e–f).

Recycle studies were conducted using **2b** to catalyse the catalytic hydrolytic evolution of DMAB to assess its activity profile as a function of reuse and thereby determine its longevity and potential for integration into a flow-based system. The practical challenges encountered with filtering and recovering the small quantity of catalyst required for these reactions (2.0 mg, 0.25 mol%) meant that it was not feasible to conduct a recycle study on this scale. Thus, a catalytic reaction using 2 mol% **2b** to hydrolyse 20 mL of 0.027 M DMAB was monitored until gas evolution ceased after which the aqueous solution was charged with an additional portion of DMAB, and the progress of the reaction monitored; this sequence was repeated to chart the hydrogen evolution

against time as a function of run number. The resulting data in Fig. 10a shows the hydrogen evolution time profile as a function of run number while the initial TOFs in Fig. 10b were determined from the first 3 min of the hydrolysis to provide a reliable comparison of the initial rates between successive runs. While high conversions were obtained across five reuses (84–88%), the initial TOF increased from 505 h^{-1} in the first run to 781 h^{-1} in the second run but then remained relatively constant in subsequent runs (Fig. 10b), retaining 97% of its initial activity across the next 4 runs. Such an increase in activity during the first run could be due either to reduction of surface ruthenium oxide species increasing the number of active sites or a structural change. Good conversions and stable activity profiles during reuse have also been reported for the catalytic hydrolytic evolution of hydrogen from DMAB using supported nanoparticles including ultrafine RuNPs anchored on porous g-C$_3$N$_4$, [230], cellulose [54], PVP [56] and Amberlyst-15 [226–239], nickel-polymer nanogel hybrid particles [47], reduced graphene oxide decorated with monodisperse RuCu alloy nanoparticles [45] whereas the initial activity of ceria supported RuNPs [52], PVP supported Ru and RuNi nanoparticles [41, 57] and monodisperse PdNPs as well as bimetallic PdCo and PdRu nanoparticles anchored on graphene oxide [44, 46, 58] all showed a significant reduction in activity across four or five reuses.

The heterogenous nature of the active species was investigated with a hot filtration study in which a catalytic hydrolysis of 0.27 M DMAB using 0.25 ml% **2b** was allowed to reach *ca.* 50% conversion after which the reaction mixture was then filtered through a syringe filter and the evolution of hydrogen from the recovered filtrate monitored for a further 30 min. Figure 11a shows that there was no evidence of post filtration gas evolution which is a strong indication that the active ruthenium species had been removed by the filtration. In a separate parallel hot filtration test, a catalytic hydrolysis of 0.27 M DMAB was allowed to reach completion and the reaction mixture subsequently filtered through a syringe

Fig. 10 **a** Plot of volume of hydrogen liberated against time for the catalytic hydrolysis of 0.027 M DMAB using 2 mol% **2b** to map catalyst performance during a reusability study across 5 runs; **b** initial TOF in mole$_{H2}$.mol$_{Ru}$$^{-1}$.h^{-1} for each run. Volumes are an average of two runs. *Conditions:* 0.54 mmol DMAB (0.032 g), 2 mol% **2b** (0.0149 g, 0.0103 mmol), water (20 mL), 303 K

Fig. 11 **a** Hot filtration test for the hydrolysis of 0.27 M DMAB catalysed by 0.25 mol% **2b** showing that the activity is quenched after filtering at t = 12 min. Red line – reaction in the presence of catalyst; blue line – reaction catalysed by **2b** and filtered at t = 12 min. **b** Sizing histogram of RuNPs for **2b** after 5 hydrolysis cycles. **c-d** TEM images of the material
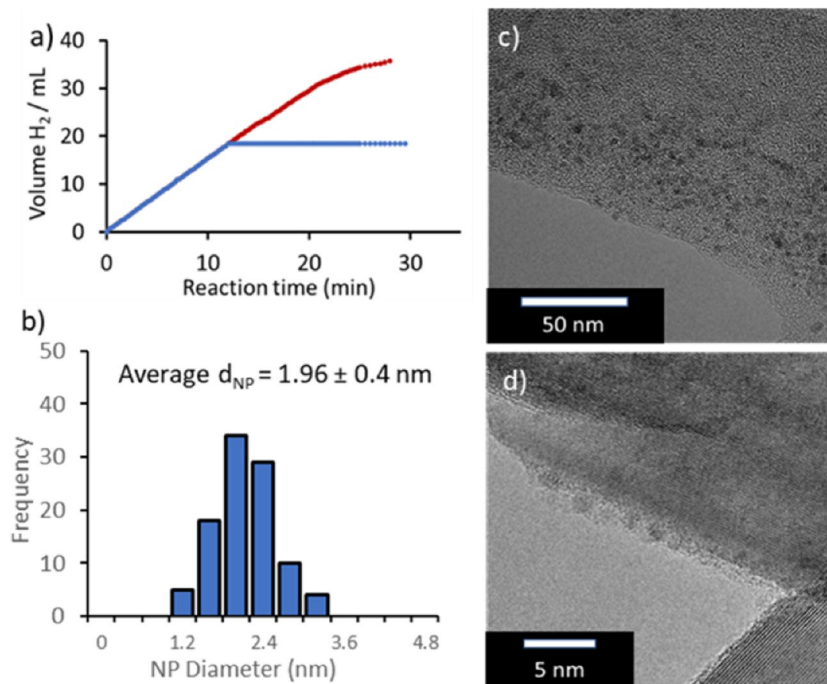
filter, the filtrate was then re-charged with an additional portion of DMAB, and the gas evolution monitored. The amount of hydrogen liberated after filtration was quantified and found to correspond to background hydrolysis, providing additional support that the active species was heterogeneous. Moreover, the ruthenium content of the aqueous phase retrieved after the hot filtration was below the detection limit of the ICP-OES (< 0.1 mg L^{-1}), which also suggests that leaching of the ruthenium to generate inactive or less active homogeneous species is unlikely. However, these experiments do not differentiate between heterogeneous catalysis at defect sites on the surface of the NP and homogeneous catalysis via a process involving rapid leaching to generate active homogeneous species that are subsequently redeposited. While the PEG-modified imidazolium component was designed with a C2-methyl substituent to prevent the formation of metal carbenes, we cannot unequivocally exclude the formation of an abnormal N-heterocyclic carbene (aNHC) species [260] from the leached ruthenium which would then be supported and retained by the polymer; as such there would be no apparent leaching of the metal as it would all be immobilised in the form of RuNPs and molecular carbene species. To this end, there have been numerous reports of the serendipitous formation of ruthenium-based abnormal carbenes during the attempted synthesis of normal N-heterocyclic carbene complexes as well as targeted synthesis for applications in catalysis as their strong σ-donor character is expected to improve performance [261–266]. Finally, TEM analysis of the catalyst recovered after the 5th run revealed that the nanoparticles remained near monodisperse with a mean diameter

of 1.96 ± 0.4 nm, comparable to that of 2.46 ± 0.4 nm for freshly prepared **2b**, confirming that agglomeration does not occur and that leaching and re-deposition is unlikely as this would probably result in an obvious change in the size and/ or distribution of the NPs (Fig. 11b-d).

3 Conclusions

In conclusion, a systematic comparison of the efficacy of amino-modified PIIL stabilised platinum and ruthenium nanoparticles as catalysts for the hydrolytic evolution of hydrogen from DMAB and AB and NABH$_4$ has been undertaken. Interestingly, while the RuNP@NH$_2$-PEGPIILS is significantly more active than its platinum counterpart for the hydrolysis of DMAB and AB, both catalysts gave comparable initial TOFs and conversions for the hydrolysis of NaBH$_4$. Kinetic studies revealed that the hydrolysis of DMAB, AB and NaBH$_4$ were all first order in catalyst and substrate. The apparent activation energies of 55.7 kJ mol^{-1} and 27.9 kJ mol^{-1} for the hydrolysis of DMAB and AB, respectively, with RuNP@NH$_2$-PEGPIILS as the catalyst are significantly lower than those of 74.6 kJ mol^{-1} and 35.7 kJ mol^{-1} for its platinum counterpart, which is consistent with the markedly higher initial TOFs obtained with the RuNPs for both substrates. Moreover, both activation energies for the hydrolysis of AB are markedly lower than the respective activation energies for the hydrolysis of DMAB which is consistent with the markedly higher rates of hydrogen evolution from

the former. In stark contrast to the hydrolysis of DMAB and AB, both catalysts gave comparable initial rates for the hydrolysis of $NaBH_4$ which was supported by their similar apparent activation energies. One of the remaining challenges hampering the implementation of sodium borohydride for hydrogen storage is the need to close the loop by effecting its regeneration from the hydrolysis product, $NaBO_2$. To this end, facile regeneration of $NaBH_4$ has recently been achieved by reacting $NaBO_2$ with CO_2 to form $Na_2B_4O_7.10H_2O$ and Na_2CO_3 both of which can be ball-milled with magnesium under ambient conditions to afford $NaBH_4$ in high yield [267]. This is an efficient, low-cost procedure compared to previously reported methods which either require an expensive reducing agent such as MgH_2, an energy intensive dehydration step or a high pressure of hydrogen [26]. As the modular synthesis of the PIIL support will facilitate further diversification we will next explore the influence of varying the amine and its loading as well as the ionic environment, porosity, and hydrophilicity on catalyst efficacy. Catalyst modifications coupled with *in operando* surface studies and the synthesis of multimetallic nanoparticles will also be the focus of future endeavours to develop a detailed understanding of this system and to identify more active and robust catalysts for use in scale-up.

Authors Contribution Simon Doherty: Conceptualization, Methodology, Supervision, Writing—original draft, Project Administration, Validation. Adhwa Alharbi: Investigation, Formal Analysis. Corinne Wills: Investigation, Resources, Formal analysis. Casey Dixon: Investigation, Formal Analysis. Elisabetta Arca: Supervision, Writing – Review and Editing, Visualization, Formal Analysis, Validation. Thomas W. Chamberlain: Supervision, Writing – Review and Editing, Visualization, Validation, Resources. Anthony Griffiths: Investigation, Visualization, Formal Analysis. Han Yan: Investigation, Visualization, Formal Analysis. Sean M. Collins: TEM Investigation, Supervision. Kejun Wu: TEM Investigation, Supervision. Richard A. Bourne: Supervision, Writing – Review and Editing. Julian G. Knight: Supervision, Writing—Review and Editing, Validation, Formal Analysis.

Declarations

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