

This is a repository copy of *Efficient hydrogen evolution from sodium borohydride* catalysed by amine-decorated cross-linked polymer immobilised ionic liquid stabilised palladium nanoparticles.

White Rose Research Online URL for this paper: <u>https://eprints.whiterose.ac.uk/225986/</u>

Version: Accepted Version

Article:

Doherty, S., Knight, J.G., Begum, T. et al. (6 more authors) (2025) Efficient hydrogen evolution from sodium borohydride catalysed by amine-decorated cross-linked polymer immobilised ionic liquid stabilised palladium nanoparticles. Canadian Journal of Chemistry. ISSN 0008-4042

https://doi.org/10.1139/cjc-2024-0257

© 2025 The Authors. This is an author produced version of an article published in Canadian Journal of Chemistry. Uploaded in accordance with the publisher's self-archiving policy.

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



1	Efficient Hydrogen Evolution from Sodium Borohydride Catalyzed by
2	Amine-Decorated Cross-Linked Polymer Immobilized Ionic Liquid
3	Stabilized Palladium Nanoparticles
4	
5	
6	Simon Doherty ^a , Julian G. Knight ^a , Tahmina Begum ^a , Reece Paterson ^a , Corinne Wills ^a ,
7	Elisabetta Arca ^b , Richard A. Bourne ^c , Han Yan ^c , Thomas W. Chamberlain ^c
8	
9	Dedication. This article is dedicated to the memory of Professor Stephen A. Westcott, a great
10	ambassador for chemistry in Canada and across the globe, Godfather to my daughter, Lucia
11	Erin and the best and most sincere of friends; you are greatly missed but with fond memories
12	that will always be cherished.
13	
14	^a Newcastle University Centre for Catalysis (NUCAT), School of Chemistry, Bedson Building,
15	Newcastle University, Newcastle upon Tyne, NE1 7RU, UK.
16	^b School of Mathematics, Statistics and Physics, Newcastle University, Newcastle Upon Tyne,
17	NE17RU, UK.
18	^c School of Chemistry and School of Chemical and Process Engineering, University of Leeds,
19	Woodhouse Lane, LS2 9JT, UK.
20	Corresponding Authors: Simon Doherty (email: <u>simon.doherty@newcastle.ac.uk</u>); Thomas W.
21	Chamberlain (email: <u>t.w.chamberlain@leeds.ac.uk</u>)

23 Abstract

Palladium nanoparticles stabilised by confinement in crosslinked amine-decorated, polymer 24 immobilised ionic liquids catalyse the hydrolytic evolution of hydrogen from NaBH4 under 25 mild conditions. A series of three PIIL supports NH_2 -Im_xPIIL (x = 1, (2a); x = 2, (2b), x = 3, 26 (2c); where x corresponds to the number of imidazolium cations in the repeat unit) were 27 28 prepared with an increasing number of imidazolium cations such that bis(styryl)-based crosslinkers 1a and 1b contain one and two imidazolium cations, respectively, while 1c is a 29 more extensive tris(styryl)-based crosslinker with three imidazolium cations. The composition 30 of the support influences the performance of the corresponding $PdNP@NH_2-Im_xPIILS$ (x = 1, 31 (4a); x = 2, (4b); x = 3, (4c) as catalysts for the hydrolysis of NaBH₄ and a comparison of the 32 most efficient system against its unmodified counterpart (i.e. PdNP@H-Im2PIIL) confirmed 33 that incorporation of the surface coordinated amine improved catalyst performance. Palladium 34 nanoparticles stabilised by NH2-Im2PIIL were the most efficient catalyst and the maximum 35 initial turnover frequency of 81 mol_{H2}.molPd⁻¹.min⁻¹ is higher than the 59 mol_{H2}.molPd⁻¹.min⁻¹ 36 and 32 mol_{H2}.molPd⁻¹.min⁻¹ obtained with PdNPs supported by NH₂-Im₁PIIL and 37 NH₂-Im₃PIIL, respectively, as well as the 19 mol_{H2}.molPd⁻¹.min⁻¹ obtained with commercial 38 10 wt% Pd/C. The results of kinetic studies, apparent activation energies and deuterium isotope 39 effects have been compared with those in the literature and support a mechanism involving rate 40 41 limiting activation of an O-H bond in water. Catalyst reuses studies showed that PdNP@NH2-Im2PIIL recycled with remarkable efficiency as high conversions were 42 maintained across five runs with the catalyst retaining over 92% of its initial activity, an 43 improvement on the 70% retention of activity with palladium nanoparticles supported by linear 44 amine-modified imidazolium-based polymer, which demonstrates the beneficial effect of 45 introducing crosslinking. 46

- 47 Keywords: sodium borohydride catalytic dehydrogenation palladium nanoparticles amine
- 48 decorated polyionic liquid supports kinetic studies recycle

1. Introduction

There is increasing global pressure to reduce our reliance on fossil fuels as they are a rapidly 50 51 dwindling resource, and their use is also responsible for the escalating levels of atmospheric CO₂. This is having a catastrophic and detrimental impact on the earth's environment, including 52 rising global temperatures, extreme and fluctuating weather patterns, and a negative influence 53 on the earth's ecosystem.¹ As such there is an urgent need to identify alternative energy carriers 54 that are sustainable and/or renewable and that provide clean energy.² Hydrogen is among the 55 most promising of these as it has a higher gravimetric energy density than petroleum (120 kJ 56 g⁻¹ v 47 kJ g⁻¹) and can be generated by harnessing the sun's energy to drive the electrolysis of 57 water to deliver high purity green hydrogen while generating oxygen as the only by-product.³ 58 The use of green hydrogen as an energy carrier would mitigate further damage to the 59 60 environment as it is carbon-free and the only by-product from its use in a fuel cell would be water.⁴ However, hydrogen is highly flammable, forms explosive environments and has a very 61 low volumetric energy density of 5.6 MJ L⁻¹, which presents major challenges for secure and 62 safe storage as well as handling and transportation. These challenges will need to be addressed 63 if the use of hydrogen and fuel cell technology in stationary, portable and transport applications 64 is to become commercially viable.⁵ Potential solutions include reversible adsorption of 65 hydrogen into the channels of a porous material,⁶ or the controlled release from low molecular 66 weight solid-state or liquid chemical hydrogen storage materials.⁷ One of the most widely 67 studied materials for hydrogen storage is sodium borohydride (NaBH₄)^{8a-d} as it is a stable solid 68 with a high storage capacity of 10.8 wt%, that exceeds the minimum target of 5.5% set by the 69 US Department of Energy (DOE), is non-toxic, inexpensive, water soluble and can be 70 71 regenerated from its hydrolysis product in high yield by a relatively straightforward protocol.^{8e} While sodium borohydride releases hydrogen when heated, this is not practical for portable 72 applications as it is stable up to 400 °C and although its hydrolysis is exothermic, it is slow and 73

74 requires a catalyst to accelerate the release of H₂. To this end, considerable effort has been dedicated towards developing cost effective catalysts for the controlled release of hydrogen 75 under mild conditions.⁹ While numerous homogeneous catalysts have been reported to catalyse 76 77 this hydrolysis and high activities have been achieved, they often suffer from poor long-term stability, require costly supporting ligands and can be difficult to recover and recycle.¹⁰ 78 Nanoparticles are also attracting considerable attention as catalysts for the evolution of 79 80 hydrogen from boron hydrides as their efficacy can be controlled through their size and morphology as well as specific metal-support interactions and the catalyst can be recovered 81 and recycled or integrated into a continuous flow platform.¹¹ However, small nanoparticles are 82 inherently unstable with respect to aggregation to larger less active species and must be 83 stabilised for use in catalysis.¹² The most common approach to prevent or limit aggregation 84 and improve the stability of nanoparticles is by encapsulation or immobilisation on supports 85 such as porous carbon structures,¹³ zeolites,¹⁴ oxides,¹⁵ mesoporous silicas,¹⁶ porous organic 86 polymers,¹⁷ metal organic frameworks,¹⁸ and most recently click dendrimers.¹⁹ This approach 87 88 has proven particularly effective and there are numerous examples of supported noble and non-noble metal nanoparticles that catalyse the hydrolysis of NaBH₄ with high initial TOFs, 89 the most active of which are RuNPs confined in zeolite-Y and PVP-stabilised RuPd 90 nanoparticles, with initial TOFs of 550 mol_{H2}.molRu⁻¹.min⁻¹ and 762 mol_{H2}.molcat⁻¹.min⁻¹, 91 respectively.^{14d,20} Moreover, there is now increasing evidence that an organic modifier and/or 92 93 ligand on the support can form a metal-organic interface with the nanocatalyst and enhance its performance by controlling the size and morphology of NPs, providing additional stabilisation 94 and preventing overgrowth or aggregation, modulating the surface electronic properties to 95 96 control adsorption/desorption of reagents and intermediates, controlling access of substrates through steric effects or through selective interaction with a functional groups or tailoring the 97 hydrophilic or hydrophobic environment and thereby the solubility of reactants.²¹ 98

We have recently been exploring the effectiveness of heteroatom-donor modified 99 polymer-immobilised ionic liquids as supports for NP catalysts on the basis that the weak 100 electrostatic stabilization provided by the covalently attached ionic liquid fragment would be 101 supplemented by a covalent interaction between the heteroatom donor and the NP surface.²² 102 Moreover, covalent attachment of the ionic liquid and the heteroatom donor to the polymer 103 should combine effective stabilisation with the favourable characteristics of grafting to a 104 support *i.e.* immobilise the ionic liquid and prevent leaching, facilitate separation, recovery, 105 and reuse of the catalyst, and reduce the amount of ionic liquid required as the NPs would be 106 107 embedded within the polymer immobilised ionic liquid. In addition, the evolving emphasis on the beneficial impact of ligands on the performance of nanocatalysts described above²¹ suggests 108 that the steric and electron donor properties of the heteroatom in polymer immobilised ionic 109 liquids could enable reaction- and/or substrate-specific catalysts to be developed and their 110 efficacy optimised and, in this regard, could be exploited in the development of new catalyst 111 technology. 112

Despite the growing number of reports of support-grafted ionic liquids for the 113 stabilisation of nanoparticles and their applications as catalysts,²³ including CO₂ 114 hydrogenation,²⁴ C-C coupling,²⁵ selective oxidations,²⁶ reductions,²⁷ and additive-free 115 hydrogen generation from formic acid,²⁸ there are only a handful of examples of their use as 116 117 catalysts for the hydrolytic dehydrogenation of hydrogen-rich boron compounds. For example, ultrafine highly dispersed AuPd nanoparticles stabilised by an imidazolium-based organic 118 polymer catalyse the dehydrogenation of amine borane more efficiently than either of the 119 monometallic counterparts,²⁹ imidazolium-modified mesoporous silica stabilised PdNPs 120 catalyse the hydrolysis of NaBH₄ and retain their efficacy across five reuses,³⁰ and polyionic 121 liquid-supported RuNPs catalyse the reductive dehydrogenation of DMAB in the synthesis of 122 benzimidazole from CO₂ and 1,2-diamines and the DMAB-mediated reduction of 123

nitroaromatic compounds and olefins.³¹ As part of our research programme to explore the use 124 of heteroatom donor modified PIILs as supports for the stabilisation of nanoparticles, we 125 recently reported that ruthenium and platinum nanoparticles stabilised by amine-decorated 126 PIILs catalyse the dehydrogenation of NaBH₄ and DMAB.³² With the aim of exploring the 127 influence of increasing the extent of crosslinking on the stability profile and longevity of the 128 nanoparticles, the performance of PdNPs stabilised by amine-decorated PIILs derived from 129 130 4-aminostyrene and imidazolium-based bis- and tris-crosslinkers as catalysts for the hydrolysis of NaBH₄ was compared against PdNPs stabilised by linear amine-decorated 131 132 imidazolium-based polymer as well as unmodified imidazolium/styrene-based polymer immobilised ionic liquid. Herein, we report our preliminary results from this study which 133 demonstrate that PdNPs stabilised by amine-decorated crosslinked imidazolium-based polymer 134 immobilised ionic liquids are more active than PdNPs supported on unmodified imidazolium-135 styrene-based polymer and that the most efficient catalyst retained over 92% of its activity 136 across five reuses. Kinetic studies and deuterium isotope effects were used to explore the 137 mechanism, and the data is consistent with rate limiting activation of the O-H bond in water 138 coupled with rapid transfer of hydride from the borohydride. While functionalisation of a high 139 surface area support has been shown to have a beneficial effect on the performance of the 140 embedded metal nanoparticles as a catalyst for the dehydrogenation of amine boranes 141 compared with their unmodified counterpart,³³ to the best of our knowledge there do not appear 142 to be any reports of the use of an amine-modified polyionic liquid as a support for the 143 stabilisation of palladium NPs for the catalytic hydrolytic dehydrogenation of hydrogen-rich 144 boron compounds. 145

146

148 **2.** Results and Discussion

149 2.1 Synthesis and Characterisation of Amine-Decorated Cross-Linked PIIL 2a-c, 150 Tetrachloropalladate Loaded Precatalysts 3a-c and PIIL Stabilized PdNP Catalysts 4a-c.

Crosslinkers 1a-c and the corresponding amine-decorated crosslinked polymer-immobilised 151 ionic liquids 2a-c employed in this project are shown in Figure 1. Crosslinkers 1a-c were 152 prepared by quaternisation of 1-(4-vinylbenzyl)-2-methyl imidazole with the appropriate 153 electrophile 4-bromomethylstyrene for 1a, 1,4-bis(bromomethyl)benzene for 1b and 154 1,3,5-tris(bromomethyl)benzene for 1c and their identity and purity were established using ${}^{1}H$ 155 and ¹³C NMR spectroscopy, FT-IR spectroscopy, mass spectroscopy and elemental analysis, 156 full details of which are provided in the supporting information. The corresponding 157 158 co-polymers **2a-c** were prepared by an AIBN initiated radical polymerisation of **1a-c** with the appropriate amount of 4-aminostyrene in ethanol at 80 °C. To this end, the 1:1, 1:2 and 1:3 159 ratios of crosslinker to 4-aminostyrene shown in Figure 1 were chosen such that complete 160 exchange of the halide for the tetrachloropalladate anion would afford precursors with an amine 161 to palladium ratio of two as this would enable a direct and meaningful comparison of their 162 performance as catalysts to be conducted. 163

The tetrachloropalladate- based precatalysts $PdCl_4(a)NH_2$ -Im_xPIILS (x = 1, (3a); x = 2, 164 (3b); x = 3, (3c)) were prepared by exchange of the halide in 2a-c with an appropriate amount 165 of tetrachloropalladate to afford the target Pd:N ratio of two and the corresponding PIIL 166 stabilised catalysts PdNP@NH₂-Im_xPIILS (x = 1, (4a); x = 2, (4b); x = 3, (4c)) were 167 subsequently generated by sodium borohydride-mediated reduction in ethanol. The palladium 168 169 loadings in precursors **3a-c** and catalysts **4a-c** were determined to be between 0.41-0.96 mmol g⁻¹ and 0.39-0.94 mmol g⁻¹, respectively, using ICP-OES, full details of which are provided in 170 the supporting information. 171



Figure 1. Composition of imidazolium-based crosslinkers 1a-c and the synthesis and composition of
the corresponding amine-decorated imidazolium-based crosslinked PIILs 2a-c.

176

The composition and purity of polymers **2a-c** was confirmed by ¹H NMR and solid state ¹³C NMR spectroscopy, IR spectroscopy, thermogravimetric analysis, and elemental analysis and the corresponding tetrachloropalladate precursors **3a-c** and their derived PdNPs **4a-c** were characterised by a combination of techniques including solid state NMR spectroscopy, TGA, SEM, TEM, XPS, IR spectroscopy, and ICP-OES (see supporting information for further details). The solid state ¹³C NMR spectra of **2a-c** and **3a-c** each contain a series of characteristic resonances between δ 116 and 145 ppm associated with the carbon

atoms of the aromatic and imidazolium rings while higher field resonances between δ 11 and 184 52 ppm correspond to the methyl group attached to C2 of the imidazolium ring, the saturated 185 backbone derived from the styrene and the methylene carbon atoms of the imidazolium-benzyl 186 unit; the solid state ¹³C NMR spectra of **3a-c** also map closely to those of their precursors. 187 188 Thermogravimetric analysis of polymers 2a-c showed an initial weight loss between 50 °C and 110 °C associated with the removal of a minor amount of physiosorbed ethanol and/or water 189 followed by two major degradation processes between 250-600 °C (Figures S19, S25, S31); 190 this stability profile confirms that these polymers are suitable as supports for the stabilisation 191 of nanoparticles for use in catalysis. 192

193 Surface characterisation of the tetrachloropalladate-loaded precursors 3a-c was undertaken by analysing the core electron excitation of nitrogen and palladium with X-ray 194 photoelectron spectroscopy (XPS) to explore possible interactions between the amine and 195 196 palladium. The discussed binding energies (BE) have not been rescaled with respect to an internal or external reference; instead, peak assignments relied on the comparison of BE 197 separations (further details are provided in the SI). Examination of the local nitrogen 198 environment of polymers 2a-c showed two peaks at 397.4 eV and 395.0 eV, which correspond 199 to the nitrogen environments in the imidazolium ring and the amine, respectively. Following 200 201 impregnation of **2a-c** with the tetrachloropalladate anion there was no discernible shift of the imidazolium N 1s peak of each of the precatalysts, **3a-c**, which suggests that there is no 202 interaction between the palladium and the nitrogen atoms of the imidazolium ring. Interestingly 203 though, analysis of the N 1s region of **3a-c** revealed the appearance of an additional component 204 at ca. 396.0 eV in each sample examined, which we have assigned to a Pd-N interaction 205 involving donation of electron density from nitrogen to palladium and a consequent shift of the 206 N 1s peak to higher binding energy relative to their supports 2a-c (Figure 2 top). This 207 interaction is consistent with our previous report of aniline-decorated PdNP catalysts for CO₂ 208

hydrogenation,^{22g} and such interactions have previously been described in the deconvolution 209 of N 1s data in other works.^{34a-c} Quantitative analysis of the N 1s components was undertaken 210 to estimate the proportion of amine that coordinated to palladium species in precatalysts **3a-c**, 211 which were all between 20-25%. Analysis of the Pd 3d core level for 3a-c revealed two Pd 212 3d_{3/2} and 3d_{5/2} doublets consistent with presence of two Pd 3d electronic environments as well 213 as a shake-up satellite line at 341.0 eV (Figure 2 bottom). The major doublet with a $3d_{5/2}$ 214 binding energy (BE) of 333.6 eV most likely corresponds to Pd(II) chloride species.^{34d} while a 215 minor component with slightly higher $3d_{5/2}$ binding energy of 335.2 eV is assigned to palladium 216 217 coordinated to amine; a shift to higher binding energy after coordination to the amine indicates that the palladium species is more electron deficient. Although coordination of a heteroatom 218 donor to a metal often results in an increase in the electron density at the metal and a consequent 219 220 shift of the 3d peaks to lower BE, shifts to higher binding energy have been reported and attributed to strong metal support interactions.^{34e} Alternatively this shift may reflect the change 221 in the coordination environment and/or a lower charge at palladium resulting from substitution 222 of chloride for amine in [PdCl₄]²⁻. The palladium 3d core level of the nanoparticles **4a-c** 223 generated by reduction of **3a-c** with NaBH₄ typically contained two pairs of $3d_{5/2}$ and $3d_{3/2}$ 224 doublets; the pair with a $3d_{5/2}$ binding energy of 331.6 eV belong to Pd(0),^{34f} while that with a 225 higher 3d_{5/2} binding energy of 333.5 eV correspond to divalent palladium, indicating that 226 reduction of the precatalyst to Pd(0) was not complete. 227

Interestingly, analysis of the N 1s region of the XPS spectra of catalyst **4a-c** revealed a dramatic reduction in the imidazolium nitrogen content compared with their supports **2a-c** and precatalysts **3a-c**. Quantitative analysis of the N 1s components determined that the relative contribution of imidazolium nitrogen atoms to the N 1s region decreased by 52-67 at.%. This loss of imidazolium appears to occur during the sodium borohydride-mediated reduction of precatalysts **3a-c** to the corresponding PdNPs **4a-c**. While we have recently discovered that the

benzylic imidazolium fragment of amine-decorated polymer immobilised ionic liquids is 234 susceptible to cleavage during their use as supports for the PdNP catalysed reduction of carbon 235 dioxide, loss of imidazolium resulting from treatment with sodium borohydride is more 236 surprising.^{22g} At this stage we tentatively suggest that this loss is also due to cleavage of the 237 benzyl-nitrogen bond in much the same manner as benzyl protecting groups are removed using 238 palladium catalysed hydrogenation. However, we cannot exclude reduction of the imidazolium 239 ring to a cyclic amine as this would also shift the N 1s peaks to lower binding energy and result 240 in a decrease in the imidazolium content. The Pd 3d core level of catalysts 4a-c typically 241 242 contained two pairs of $3d_{5/2}$ and $3d_{3/2}$ doublets; those with $3d_{5/2}$ binding energies of 331.6-331.7eV corresponding to Pd(0) while the pair with 3d_{5/2} BE's of 333.4-333.5 eV correspond to 243 divalent palladium, indicating that reduction to Pd(0) is not complete (Table S6). Incomplete 244 reduction may be associated with Pd(II) species strongly coordinating to Lewis basic donors 245 which would limit their reducibility.^{34a} To this end, qualitatively, there is a greater proportion 246 of Pd(0) compared with Pd(II) species in 4a than either 4b or 4c; this could be attributed to the 247 higher amine to palladium ratio as a higher amine loading would necessarily influence the 248 number of Pd(II)-amine interactions and thereby the extent of reduction. It is unlikely that the 249 divalent Pd species is due to the presence of PdO as the Pd(II)-Pd(0) BE separation of ca. 1.8 250 eV is much larger than the 1.35 eV or even 0.65 eV observed previously for PdO-Pd(0) 251 mixtures.^{34g,h} However, the full-width at half maximum values of the Pd(II) species in catalysts 252 4a-c are 1.5 times larger than those measured for 3a-c, therefore a more complicated mixture 253 of species is probable. 254

255

256



Figure 2. N 1s core level XPS spectra (top) and Pd 3d XPS spectra (bottom) of tetrachloropalladate
based precatalysts PdCl₄@NH₂-Im_xPIILS (3a-c).

TEM micrographs of 4a-c revealed that the palladium nanoparticles are near 262 monodisperse with average diameters of 3.67 ± 0.99 nm (4a), 2.13 ± 0.51 nm (4b) and $2.76 \pm$ 263 0.93 nm (4c). Representative micrographs and associated distribution histograms based on the 264 sizing of at least 100 particles are shown in Figure 3. To this end, there have been numerous 265 reports in which a Pd---N interaction involving an amine-modified support appears to play an 266 important role in the growth of small highly dispersed nanoparticles. Examples with mean 267 diameters similar to those in 4a-c include aminopropyl functionalised SBA-15 (1.5–1.6 nm),³⁵ 268 amide and pyridine functionalised porous organic copolymers (1.9–2.4 nm),³⁶ amine-modified 269 activated carbon,³⁷ amine-modified reduced graphene oxide,³⁸ amine-modified mesoporous 270 silica (2.3–3.48 nm)³⁹ nitrogen-doped carbon and carbon nanotubes,⁴⁰ and diamine alkalised 271 reduced graphene oxide.41 272



Figure 3. (a, c, e) High resolution TEM images of PdNPs for PdNP@NH₂-Im_xPIILS (4a-c),
respectively, and (b, d, e) the corresponding size distribution determined by counting > 100 particles.
N.B. White scale bar is 10 nm in all cases.

289 2.2 PdNP Catalysed Hydrolytic Evolution of Hydrogen from NaBH4

Having recently explored the efficacy of amine-decorated imidazolium-based polymer immobilised ionic liquid stabilised Ru and Pt nanoparticles as catalysts for the hydrolytic evolution of hydrogen from NaBH₄,^{22h,32a-b} the project was extended to explore the influence on catalyst performance of increasing the extent of crosslinking in the amine-decorated PIIL support in order to develop a catalyst with a stable activity profile and good mechanical integrity for integration into a continuous flow system. Preliminary comparative studies were

conducted using 0.35 mol% of 4a-c to catalyse the hydrolysis of 20 mL of 0.028 M NaBH4 at 296 313 K, the results of which are presented graphically in Figure 4. The progress of the reaction 297 298 was monitored by measuring the amount of water displaced from an inverted burette assembly to quantify the volume of hydrogen liberated as a function of time. Under these conditions, 299 hydrogen evolution started instantaneously upon addition of the NaBH₄ *i.e.* there was no 300 apparent induction which is consistent with catalysis by the preformed metallic PdNPs. All data 301 302 were corrected by subtracting the volume of hydrogen liberated under the same conditions at the same time intervals but in the absence of catalyst. The data in Figure 4 shows that 4a and 303 304 4b are more efficient catalysts for the hydrolytic evolution of hydrogen from NaBH₄ than 4c as evidenced by the initial TOFs of 59 and 81 mol_{H2}.molPd⁻¹.min⁻¹ for 4a and 4b, respectively, 305 compared with 32 mol_{H2}.molPd⁻¹.min⁻¹ for 4c. The influence of the amine on catalyst efficacy 306 307 was explored by comparing the performance of 4b against PdNPs stabilised by unmodified polymer generated by the copolymerisation of crosslinker 1b with styrene in place of 308 4-aminostyrene *i.e.* H-Im₂PIIL.^{22c} Under otherwise identical conditions, **4b** was markedly more 309 active than its unmodified counterpart as evidenced by the TOF of 45 mol_{H2}.molPd⁻¹.min⁻¹. 310 While this modification alone suggests that removal of the amine could be responsible for the 311 reduction in activity, it will be necessary to explore further modifications and conduct a more 312 thorough investigation to establish the influence of the amine loading (amine to IL ratio), the 313 type of amine and the amine to palladium stoichiometry on catalyst efficiency and thereby 314 understand how polymer composition influences catalyst performance. The efficacy of 4a-c as 315 catalysts for the hydrolytic evolution of hydrogen from NaBH4 was also compared with 316 commercially available 5 wt% Pd/C and 10 wt% Pd/C and the initial TOFs of 23 317 mol_{H2}.molPd⁻¹.min⁻¹ and 19 mol_{H2}.molPd⁻¹.min⁻¹, respectively, are significantly lower than 318 those obtained with 4a-c. In addition, pre-stirring 5 μ mol of Pd/C with a homogeneous aqueous 319 solution of each of the polymers **2a-c** for 12 h prior to addition of the NaBH₄ only resulted in 320

a slight improvement in the initial TOF compared with the same loading of Pd/C but in the absence of **2a-c**.



Figure 4. Hydrolytic release of hydrogen from NaBH₄ as a function of time at 313 K catalysed by 0.35
mol% of 4a-c, PdNP@H-Im₂PIIL and commercial 5 wt% Pd/C and 10 wt% Pd/C and their
corresponding initial TOFs.

327

While comparisons of catalyst performance to literature reports must be treated with 328 an element of caution due to the disparate conditions and the lack of standard protocols, a 329 survey of relevant studies revealed that the TOF of 81 mol_{H2}.molPd⁻¹.min⁻¹ obtained with **2b** 330 appears to be among the highest reported for the aqueous phase dehydrogenation of sodium 331 borohydride catalyzed by a monometallic palladium nanoparticle-based catalyst. For example, 332 this initial TOF is significantly higher than that of 2.2 mol_{H2}.molPd⁻¹.min⁻¹ reported for click 333 dendrimer supported PdNPs,^{19a} 10.9 mol_{H2}.molPd⁻¹.min⁻¹ (23.0 mLmin⁻¹gcat⁻¹) obtained at 295 334 K with palladium nanoparticle multiwalled carbon nanocomposites, ^{13f} 4.6 mol_{H2}.molPd⁻¹.min⁻¹ 335 for ultrasmall palladium nanoparticles stabilised in beta-cyclodextrin derived organo-nanocup 336 capping agents,⁴² 14.6 mol_{H2}.molPd⁻¹.min⁻¹ (2.4 \pm 0.3 x 10⁻⁴ s⁻¹) with 10 % Pd/C,⁴³ and 7 337 mol_{H2}.molPd⁻¹.min⁻¹ obtained at 295 K with palladium mesoporous carbon composite,^{13e} 338

although it is lower than the 348 mol_{H2}.molPd⁻¹.min⁻¹ reported for CoFe₂O₄ modified PdNPs,⁴⁴ 339 and 495 mol_{H2}.molPd⁻¹.min⁻¹ for palladium nanoclusters supported by partially decomposed 340 porous ZIF-67,⁴⁵ as well as 263.4 and 762 mol_{H2}.molPd⁻¹.min⁻¹ obtained with a bimetallic 341 magnetic Co-Pd/C nanocomposite⁴⁶ and PVP stabilized RuPd nanoparticles,²⁰ respectively. As 342 the PIIL based precursors are prepared by anion exchange-based impregnation this method is 343 currently being applied to prepare precatalysts with well-defined stoichiometries of noble and 344 non-noble metals to develop multimetallic NPs and investigate their composition-performance 345 profiles to identify more cost-effective catalysts for optimisation. 346

347

348 2.3 Kinetic Studies on the Hydrolytic Evolution of Hydrogen from NaBH4

The disparate initial TOFs obtained with 4a-c prompted us to investigate the kinetics of 349 hydrolysis as a function of temperature to determine the activation parameters for the release 350 of hydrogen from NaBH₄ and to compare the data with related literature reported systems. A 351 series of reactions were conducted to determine the initial rates of hydrolysis as a function of 352 time across a narrow range of temperatures from 294 K to 323 K. The apparent activation 353 energies (E_a) for the hydrolysis of 0.028 M NaBH₄ catalysed by 0.35 mol% 4a-c were 354 calculated to be 39.5 kJ mol⁻¹ (4a), 39.4 kJ mol⁻¹ (4b) and 48.5 kJ mol⁻¹ (4c), from the 355 corresponding Arrhenius plots of $\ln(k)$ against 1/T (lnk = lnA - E_a/RT) shown in Figures 5b, d 356 and f); the initial rates were calculated from the linear portion of the plots of the volume of 357 hydrogen released against time (Figure 5a, c and e). These activation energies are comparable 358 to that of 45.1 kJ mol⁻¹ recently reported for PdNPs supported over fused graphene-like material 359 (PdPGLM)⁴⁷ but slightly lower than the 62.7 kJ mol⁻¹ for palladium nanoparticle multiwalled 360 carbon nanotube composites,13f 63.1 kJ mol-1 for magnetic recyclable CoFe2O4-modified 361 PdNPs,⁴⁴ 58.5 kJ mol⁻¹ calculated for PdNPs supported by partially decomposed porous 362

363 ZIF-67,⁴⁵ and 58.9 kJ mol⁻¹ for ultrasmall palladium nanoparticles stabilised by 364 organo-nanocups,⁴² and higher than the 28.0 kJ mol⁻¹ for Pd/C,^{43b} 27.9 kJ mol⁻¹ palladium 365 mesoporous carbon composites,^{13e} 14 kJ mol⁻¹ for PdNP incorporated in mesoporous 366 MCM-41,⁴⁸ and 22.3 kJ mol⁻¹ for carbon nano tube-graphene supported PdRu.⁴⁹ The lower 367 apparent activation energies for **4a** and **4b** compared with **4c** are consistent with their efficacy 368 as the former have comparable initial TOFs which are higher than that obtained with **4c**.

The hydrolytic dehydrogenation of NaBH₄ was also investigated as a function of the catalyst 369 concentration to determine the reaction order by measuring the initial rates of hydrolysis of 20 370 mL of 0.028 M NaBH₄ at 323 K across range of catalyst concentrations from 0.7 mol% to 2.45 371 mol%. The resulting plots of the initial hydrogen generation rate against catalyst loading on a 372 logarithmic scale were all straight lines with slopes of 0.97 (4a), 0.99 (4b) and 1.02 (4c) 373 indicating that the hydrolysis is first order with respect to catalyst (Figure 6a-b and Figures 374 S2a-f in the supporting information). A survey of the relevant literature revealed that this data 375 is consistent with recent reports for the hydrolysis of boron hydrides catalysed by mono and 376 bimetallic noble metal-based NPs including Co_{0.97}Pt_{0.03}@CeO_x nanocomposite grown on 377 carbon-grafted graphene oxide (slope = 1.167),⁵⁰ PtCo@dendrimer (slope = 0.85),^{19a} magnetic 378 Co-Pd/C nanocomposite (slope = 1.173),⁴⁶ Ni₂Pt@ZIF-8 (slope = 0.82),⁵¹ 'click' dendrimer 379 stabilised PtNPs (slope = 0.88),^{19b} and a bimetallic graphene-cobalt-platinum nanohybrid 380 catalyst.52 381

382

383

384

385





Figure 5. (a), (b) and (c) Plots of volume of hydrogen liberated against reaction time for the hydrolysis of 20 mL of 0.028 M NaBH₄ across a range of temperatures catalysed by 0.35 mol% **4a**, **4b** and **4c**, respectively, and the associated Arrhenius plots for hydrolysis of NaBH₄ catalysed by (d) **4a**, (e) **4b** and (f) **4c**; the initial rates were calculated from the slopes of the fitted lines. Each hydrolysis was conducted in triplicate. Initial rates (k) = mole_{H2}.min⁻¹.



395

Figure 6. (a) Volume of hydrogen liberated as a function of reaction time for the hydrolysis of 20 mL of 0.028 M NaBH₄ catalysed by various amounts of 4b. (b) Corresponding plot of the initial hydrogen generation rate against catalyst concentration in logarithmic scale. *Conditions:* 0.56 mmol NaBH₄ (0.021 g), 0.35, 0.7, 1.05, 1.4, 1.75, 2.1, 2.45 mol% 4b, water (20 mL), 323 K. Volumes measured are an average of three runs. Initial rate (k) = mol_{H2}.min⁻¹.



403 Figure 7. (a) Volume of hydrogen liberated as a function of reaction time for the hydrolytic 404 dehydrogenation of NaBH₄ catalysed by **4b** (7.05 μ mol, 0.01 g) in water (20 mL), initial concentrations 405 of sodium borohydride ([NaBH₄]₀ = 0.35, 0.70, 1.05, 1.4, 1.75, 2.1 mM). (b) Corresponding plot of the 406 initial hydrogen generation rate against sodium borohydride concentration in logarithmic scale. 407 Volumes measured are an average of three runs. Initial rate (k) = mol_{H2}.min⁻¹.

The corresponding kinetic study to investigate the variation in the rate of hydrolysis as 408 a function of the substrate concentration was conducted at 323 K using 7.05 μ mol of 4b as 409 catalyst with initial concentrations of NaBH4 that correspond to substrate:catalyst ratios 410 between 1:1 and 6:1. Such low catalyst to hydride ratios were required for this kinetic study to 411 avoid [BH₄]⁻ induced dynamic saturation of the active sites on the catalyst surface as a high 412 sodium borohydride concentration would give zero order kinetics, as previously reported.⁵³ 413 The slope of 0.98 obtained from the logarithmic plot of the hydrogen generation rate against 414 the concentration of NaBH₄ catalysed by 7.05 µmol of 4b with initial concentrations of NaBH₄ 415 between 0.7 mM and 2.4 mM confirms that the hydrolysis is first order with respect to hydride 416 (Figure 7a-b). Similarly, under the same conditions slopes of 1.016 and 1.017 were obtained 417 with catalysts 4a and 4c, respectively, both of which are consistent with first order kinetics 418 (Figure S3a-f in the supporting information). While zero order kinetics with respect to hydride 419 concentration are commonly reported for this hydrolysis, these reactions are typically 420 conducted at high borohydride:catalyst ratios where the surface active sites are likely to be 421 422 completely saturated, kinetic studies conducted at low concentrations of hydride have been 423 reported to be first order with respect to hydride for platinum and palladium dispersed on the surface of functionalised carbon nanotubes,⁵⁴ as well as palladium and ruthenium on carbon.⁵⁵ 424

425

426 **2.4 Kinetic Isotope Effects**

Deuterium labelling studies and the kinetic isotope effect have been routinely employed to probe the catalytic hydrolysis of boron hydrides to elucidate information about the rate limiting step and several pathways have been proposed.^{19b,c,51,56,57,58} Although the kinetics of this hydrolysis are complicated it is clear that borohydride provides one of the two hydrogen atoms of the derived hydrogen gas while the other is derived from the water,^{7b,11c} and that the

rate limiting step involves activation of one of the O-H bonds in water as evidenced by a large 432 kinetic isotope effect when the hydrolysis is conducted in D₂O compared with H₂O.^{19a-c,59,60,56} 433 One of the most commonly proposed pathways involves hydrogen bond facilitated oxidative 434 addition of one of the O-H bonds in a surface coordinated [H₃B----H----OH]⁻ ensemble 435 (Scheme 1a). The hydrogen would then be liberated from the surface in a final reductive 436 elimination between the water derived NP-H and a borohydride derived NP-H, generating the 437 438 monohydroxylated borane [HO-BH₃]⁻ (Scheme 1b) which participates in subsequent hydride transfers to ultimately generate Na[BO₂]. While the borohydride derived NP-H may result from 439 440 either hydride transfer or oxidative addition of a B-H bond, hydride transfer is more likely as borohydrides are extremely powerful transfer reagents. In an alternative pathway, Jagirdar and 441 Ma have suggested that one of the O-H bonds of water is activated by a hydrogen bonding 442 interaction between water and a borohydride-derived surface coordinated hydride i.e. 443 N---H---OH (Scheme 1c-d).⁶¹ 444



Scheme 1. Possible pathway for the metal nanoparticle catalysed hydrolytic evolution of hydrogen from the hydrogen bonded array [H₃B-H-----OH]⁻ *via*; (a) rate limiting oxidative addition of an O-H bond and hydride transfer followed by (b) reductive elimination of H₂ and abstraction of a surface hydroxide to liberate [H₃B-OH]⁻; (c) rapid hydride transfer followed by (d) hydrogen bond activation of the O-H bond; Inset: HN---H----OH₂ hydrogen bond between a surface grafted amine and the [H₃B-H-----H----OH]⁻ ensemble facilitating activation of the O-H bond.

The role of H₂O in the hydrolytic evolution of hydrogen from NaBH₄ catalysed by 0.35 456 mol% 4b was explored by comparing the rates of hydrolysis of 0.028 M NaBH₄ in H₂O and 457 D₂O at 323 K. Under otherwise identical conditions comparative kinetic studies revealed that 458 the hydrolysis in H₂O was more rapid than in D₂O as evidenced by a primary kinetic isotope 459 effect ($k_{\rm H}/k_{\rm D}$) of 3.6 (Figure 8). Similar values of $k_{\rm H}/k_{\rm D}$ were obtained for reactions catalysed 460 by 4a ($k_{\rm H}/k_{\rm D} = 2.7$) and 4c ($k_{\rm H}/k_{\rm D} = 3.7$) and the corresponding data is presented graphically in 461 Figures S4a-c of the supporting information. These values indicate that rate limiting activation 462 of one of the O-H bonds in water is integral to the catalysis as they are comparable to the $k_{\rm H}/k_{\rm D}$ 463 464 value of 1.8 reported for a detailed kinetic study on the hydrolysis of NaBH₄ in alkaline media catalysed by 5 wt% Pt/C,⁵⁶ as well as values reported for NiNP@ZIF-8 ($k_{\rm H}/k_{\rm D} = 2.49$),⁵⁷ 465 dendrimer stabilised palladium nanoparticles ($k_{\rm H}/k_{\rm D} = 2.3$),^{19b} and PtCo@dendrimer ($k_{\rm H}/k_{\rm D} =$ 466 2.4).^{19c} However, this data does not distinguish between a pathway in which the hydrogen 467 bonded ensemble activates the O-H bond to generate a surface-coordinated borohydride and a 468 water derived metal hydride and one in which concerted activation of O-H and B-H bonds 469 afford borohydride and water-derived metal dihydrides. Thus, additional kinetic studies were 470 undertaken by comparing the initial rates of hydrolysis of 0.028 M NaBH₄ and NaBD₄ in H₂O 471 using 0.35 mol% 4b as the catalyst. Analysis of the initial rates obtained at 323 K under 472 conditions of catalysis gave a KIE of 1.05 (Figure 8b) and similar values were also obtained 473 with catalysts 4a and 4c (Figure S5a-c) While these values are consistent with activation of 474 only the O-H bond in the rate determining step with rapid transfer of hydride from the [BH₄]⁻ 475 to the surface of the NP, activation of the O-H bond may occur by either hydrogen bonding to 476 a surface hydride or by formation of a hydrogen bonded surface-coordinated ensemble between 477 [BH₄]⁻ and water, as described above. At this stage we favour the former as the latter might be 478 expected to manifest itself as an inverse KIE, which may become apparent through additional 479 KIE studies under stoichiometric conditions. Finally, the efficacy of 4b compared to its 480

unmodified counterpart, PdNP@H-Im2PIIL, may be associated with the formation of a HN---481 H----OH₂ hydrogen bond between a surface grafted amine on the PIIL support and the [H₃B-482 H-----H----OH]⁻ ensemble, facilitating activation of the O-H bond (Scheme 1, inset), in a 483 manner similar to that previously described for the dehydrogenation of formic acid.⁶² However, 484 further catalyst modifications to explore the influence of the polymer composition, the surface 485 amine group and its loading on catalyst performance coupled with in operando surface 486 investigations and additional kinetic studies will be required to develop a more detailed 487 understanding of how the amine effects catalyst performance. 488





Figure 8. (a) Comparison of the initial hydrogen release from 20 mL of 28 mM NaBH₄ in H₂O and D₂O
catalysed by 0.35 mol% 4b (2.8 mg) conducted at 323 K. Volumes measured were an average of three
runs. (b) Hydrogen release from 20 mL of a 28 mM solution of NaBH₄ (red line) and NaBD₄ (blue line)
conducted in H₂O at 323 K and catalysed by 0.35 mol% 4b (2.8 mg).

494

495 2.5 Catalyst Reuse Studies

The longevity and stability profile of **2b** as a catalyst for the hydrolysis of NaBH₄ was investigated using recycle studies to assess the potential for use in scale-up or for integration into a continuous flow-based system, as previously reported for the PdNP@PPh₂-PEGPIILS catalysed reduction of nitroarenes.^{22b} As a result of the practical problems associated with

isolating the small amount of catalyst typically required for a hydrolysis experiment without 500 incurring any attrition during the recovery procedure, a reuse experiment was conducted using 501 2 mol% loading of catalyst 4b and the amount of gas generated from 20 mL of 0.011 M NaBH₄ 502 was monitored as a function of time until the reaction reached completion. The aqueous 503 reaction mixture was then re-charged with an additional portion of sodium borohydride and the 504 gas evolution monitored again; this sequence was repeated to obtain a profile of the catalyst 505 506 performance as a function of reaction time and reuse number. The resulting plot of volume against time in Figure 9a shows that the catalyst retained its activity as comparable conversions 507 508 were reached at the same time across five reuses. Moreover, there was only a minor reduction in catalyst activity in successive runs, as defined by the percentage reduction in the initial rate 509 based on the slope of the linear portion of the plots in Figure 9a. The corresponding profile in 510 Figure 9b shows that 4b retained ca. 92 % of its activity across the five runs, which is an 511 improvement on the corresponding activity profile for linear amine-decorated non-crosslinked 512 polymer-immobilised ionic liquid-stabilised PdNPs, which only retained 70% of its initial 513 activity across 5 runs under otherwise identical conditions. A comparison with selected relevant 514 literature reports revealed that the activity profile obtained with 4b is comparable to or an 515 improvement on recycle studies with noble metal nanoparticle/support systems such as 516 ultrafine ruthenium nanoparticles anchored on a MOF/COF dual carrier,^{18a} ruthenium modified 517 titanium dioxide support, which retained over 80% of its activity, magnetic Co-Pd/C 518 nanocomposites,⁴⁶ palladium nanoparticles embedded on mesoporous carbon materials,^{13e} 519 "click"-dendrimer-supported synergistic bimetallic nanocatalysts,^{19a} zeolite confined 520 RuNPs,^{14d} and graphene quantum dots-transition metal nanoparticles,⁶³ each of which retained 521 between 70-95% of their initial activity up to the fifth reuse. The slight decrease in activity as 522 a function of run number may be due the change in pH, which increases with the extent of 523 hydrolysis due to formation of basic sodium borate by-product. This could be addressed in a 524

carefully engineered continuous process which would avoid build-up of borate by-product or
by using aqueous borate buffered solution to maintain the pH between 7.2 and 8, as reported
by Sneddon *et al.* for the rhodium catalysed release of hydrogen from ammonia triborane; under
these conditions the Rh/Al₂O₃ catalyst showed little change in the hydrogen release rates over
11 cycles.⁶⁴





Figure 9. (a) Plots of volume of hydrogen liberated against time for the hydrolysis of 20 mL of 0.011
M NaBH₄ catalysed by 2 mol% 4b at 323 K during the reusability study across 5 runs. (b) Conversion
reached in each run and percentage of the initial activity remaining after successive reuses. Volumes
measured were an average of three runs.

536

The heterogeneous nature of the active species was explored by conducting a pair of parallel hot filtration experiments. In the first, 0.35 mol% **4b** was used to catalyse the hydrolysis of 20 mL of 0.028 M NaBH₄ and the reaction allowed to reach *ca*. 50% conversion (*ca*. 5 min) at which point the reaction mixture was filtered through a 0.45 μ m syringe filter and the hydrogen subsequently liberated from the recovered filtrate was quantified for a further 25 min. After subtracting the background hydrolysis, the resulting data in Figure 10a shows

that there was no further measurable evolution of hydrogen indicating that filtration removed 544 the active palladium species. In the second hot filtration experiment, a hydrolysis was allowed 545 to reach completion after which the reaction mixture was filtered through a 0.46 μ m syringe 546 filter and the recovered filtrate charged with a further 1 mL portion of 0.56 M NaBH₄ and the 547 gas evolution monitored. The volume of gas liberated was quantified and found to correspond 548 closely to the background hydrolysis, which is also consistent with catalysis by a heterogeneous 549 species. Furthermore, analysis of the recovered filtrate from the second hot filtration 550 experiment revealed that the palladium content was below the detection limit of ICP-OES (<0.1 551 mg L⁻¹), providing further evidence that leaching of palladium was unlikely. However, routine 552 hot filtration tests such as these do not distinguish between catalysis at the surface of a 553 heterogeneous species and leaching-redeposition to generate an active homogeneous species, 554 although such a process may well manifest itself in a change in the size, size distribution and/or 555 morphology of the nanoparticles. To this end, TEM analysis of the catalyst recovered after the 556 5th run revealed that the nanoparticles remained near monodisperse with a mean diameter of 557 2.6 ± 0.6 nm, which is similar to that of 2.13 ± 0.51 nm pre-catalysis (Figure 10b), confirming 558 that agglomeration is not significant and that leaching and redeposition is unlikely. 559





Figure 10. Hot filtration experiment for the hydrolysis of 28 mM NaBH₄ catalysed by 0.35 mol% 4b showing that filtration of the reaction mixture at *ca*. t = 5 min quenches the activity. (a) Red line reaction in the presence of catalyst 4b and blue line - reaction catalysed by 4b and filtered at t = 5 min. (b) Sizing histogram of PdNPs for 4b after use in 5 hydrolysis runs and inset TEM image of the material, N.B. white scale bar is 20 nm.

567

568 **3** Conclusion

569 Palladium nanoparticles stabilised by a series of crosslinked amine-decorated polymerimmobilised ionic liquids catalyse the hydrolytic evolution of hydrogen from NaBH4 under 570 mild conditions and are markedly more efficient than commercial 5 wt% and 10 wt% Pd/C and 571 572 5 wt% Pd/C/NH₂-Im_xPIIL, as well as PdNPs stabilised by unmodified H-Im₂PIIL; this suggests that the surface coordinated amine plays a role in improving catalyst performance. The highest 573 TOF of 81 mol_{H2}.molPd⁻¹.min⁻¹ obtained with PdNP@NH₂-Im₂PIIL is among the highest 574 reported for the hydrolytic evolution of hydrogen from NaBH₄ catalysed by a monometallic 575 palladium nanoparticle-based system. Kinetic studies, apparent activation energies and 576 577 deuterium isotope effects are consistent with a mechanism involving rate limiting activation of one of the O-H bonds of water, while activation of the B-H bond either by hydride transfer or 578 oxidative addition appears to be rapid. At this stage we tentatively suggest that the amine may 579 580 play a cooperative role to facilitate the rate limiting cleavage of the O-H bond, although we cannot eliminate/exclude alternative explanations including modification of the surface 581 electronic structure or control of the growth and dispersion of the NPs. Reuse experiments 582 583 showed that PdNP@NH2-Im2PIIL recycled with remarkable efficiency and retained over 92% of its initial activity over five runs which is an improvement on the 70% obtained for palladium 584 nanoparticles supported by linear amine-modified imidazolium-based polymer which 585 underpins the beneficial effect of introducing the crosslinking on catalyst longevity. Although 586

NaBH₄ can deliver high-purity H₂ at room temperature with controllable kinetics *via* catalytic 587 hydrolysis it will be necessary to close the loop by effecting its regeneration from the borate 588 by-product. To this end, high yields of NaBH₄ have recently been achieved by reacting NaBO₄ 589 with CO₂ to afford Na₂B₄O₇.10H₂O and Na₂CO₃ which were both subsequently ball-milled 590 with Mg under mild conditions. This is an improvement on previous methods as it is cost 591 effective and efficient, avoids the use of expensive reducing agents such as MgH₂ and does not 592 require energy-intensive dehydration of Na₂B₄O₇·10H₂O or a high pressure of hydrogen. 593 Studies are currently underway to prepare additional polymer modifications and identify an 594 595 optimum composition to further improve catalyst activity and stability and to unequivocally establish whether the amine influences nanoparticle growth/dispersion, surface electronic 596 properties or participates in the elementary steps of the catalysis. A parallel programme has 597 598 also been initiated to explore the effect of confinement on the activity and stability of PdNPs immobilised within the pores of amine-decorated Mesoporous Ionic Liquid-Functionalised 599 Silica. 600

601 Author Statements

602 Acknowledgements

T.B gratefully acknowledges, Bangladesh Governance Innovation Unit (GIU) for a PM 603 Fellowship. R.P. acknowledges the Engineering and Physical Sciences Research Council 604 605 (EPSRC) Centre for Doctoral Training in Renewable Energy Northeast Universities (ReNU) for funding through grant EP/S023836/1. T.W.C., R.A.B. and H.Y. acknowledge the NanoMan 606 EPSRC project (EP/V055089/1) for funding. We also thank Dr Tracey Davey for the SEM 607 images (Faculty of Medical Sciences, Newcastle University) and Zabeada Aslam and the Leeds 608 electron microscopy and spectroscopy centre (LEMAS) at the University of Leeds for TEM 609 analysis. This article is dedicated to the memory of Professor Stephen A. Westcott (Canada 610 Research Chair holder in the Department of Chemistry & Biochemistry, Mount Allison 611 University, Canada) who recently passed away; a fantastic and inspired scientist, a great 612 ambassador for chemistry teaching and research in Canada and across the globe, a selfless, 613 generous, and kind human being but most of all a genuine and true friend who is greatly missed. 614

615

616 Competing interests

617 The authors declare there are no competing interests.

618

619 CRediT authorship contribution statement.

Simon Doherty: Conceptualization, Methodology, Supervision, Writing - original draft, Project
Administration, Validation. Julian G. Knight: Supervision, Writing - Review and Editing,
Validation, Formal Analysis. Tahmina Burgen: Investigation, Formal Analysis. Reece Paterson:
Formal Analysis, Validation, Writing – Review and Editing. Corinne Wills: Investigation,
Resources, Formal analysis. Elisabetta Arca: Supervision, Writing – Review and Editing,

625	Visualization, Formal Analysis, Validation. Richard A. Bourne: Supervision, Writing – Review
626	and Editing. Han Yan: Investigation, Visualization, Formal Analysis. Thomas W. Chamberlain:
627	Supervision, Writing – Review and Editing, Visualization, Validation, Resources.
628	
629	Data availability statement
630	Data generated or analyzed during this study are provided in full within the published article
631	and its supplementary materials. Synthesis and characterisation of crosslinkers (1a-c), amine
632	decorated cross-linked polymer immobilised ionic liquids (2a-c), tetrachloropalladate loaded
633	precatalysts (3a-c) and PdNP catalysts (4a-c)
634	
635	Author information
636	Author ORCIDs
637	Simon Doherty: <u>https://orcid.org/0000-0003-1103-8090</u>
638	Thomas W. Chamberlain: https://orcid.org/0000-0001-8100-6452
639	
640	

641 References

1. (a) Nejat, P.; Jomehzadeh, F.; Taheri, M. M., Gohari, M.; Abd. Majid M. Z. A global 642 review of energy consumption, CO₂ emissions and policy in the residential sector (with 643 an overview of the top ten CO₂ emitting countries). *Renew. Sustain. Energy Rev.* 2015, 644 43, 843-862. (b) Davis, S. J.; Caldeira, K. Consumption-based accounting of CO₂ 645 646 emissions. Proc. Nat. Acad. Sci. 2010, 107, 5687-5692. (c) CO₂.earth Are we Stabilizing Yet? Prooxygen Web Site https://www.co2.earth/ (accessed 20th September 647 2021). (d) Olivier, J. G. J.; Peters, J. A. H. W. Trends in global CO₂ and total greenhouse 648 gas emissions 2019 Report. J. Perera, Int. J. Environ. Res. Public Health 2018, 15, 10. 649 doi.org/10.3390/ljerph15010016. 650 2. Poizot, P.; Dolhem, F. Clean energy new deal for a sustainable world: from non-CO2 651 generating energy sources to greener electrochemical storage devices. Energy Environ. 652 *Sci.* **2011**, *4*, 2003–2019. 653 3. (a) Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. 654 Nature 2001, 414, 353–358. (b) Rodríguez-Lugo, R.E.; Trincado, M.; Vogt, M.; Tewes, 655 F.; Santiso-Quinones, G.; Grützmacher, H. A homogeneous transition metal complex 656 for clean hydrogen production from methanol-water mixtures. Nat. Chem. 2013, 5, 657 342-347. (c) He, T.; Pachfule, P.; Wu, H.; Xu, Q.; Chen, P. Hydrogen Carriers. Nat. 658 659 Rev. Mater. 2016, 16059. (d) Ball, M.; Wietschel, M. The future of hydrogen opportunities and challenges. Int. J. Hydrogen Energy 2009, 34, 615-627. (e) 660 https://www.energy.gov/eere/fuelcells/doe-technical-targets-onboard-hydrogen-661 storage-light-duty-vehicles (accessed 24th October 2023). (f) Mazloomi, K.; Gomes. 662 C. Hydrogen as an energy carrier: Prospects and challenges. Renew. Sustain. Energy 663 Rev. 2012, 16, 3024-3033. (g) Abdin, Z.; Zafaranloo, A.; Rafiee, A.; Mérida, W.; 664 Lipiński, W.; Khalilpour, K. R. Hydrogen as an energy vector. *Renew. Sustain. Energy* 665

666		Rev. 2020, 120, 109620. (h) Hirscher, M.; Yartys, V. A.; Baricco, M.; von Colbe, J. B.;
667		Blanchard, D.; Bowman, R. C.; Broom, D. P.; Buckley. C.E.; Chang, F.; Chen, P.; Cho,
668		Y. W.; Crivello, J. C.; Cuevas, F.; David, W. I. F.; de Jongh, P. E.; Denys, R. V.;
669		Dornheim, M.; Felderhoff, M.; Filinchuk, Y.; Froudakis, G. E.; Grant, D. M. et al.
670		Materials for hydrogen-based energy storage – past, recent progress and future outlook.
671		J. Alloys Compd. 2020, 827, 153548. (i) Abbasi, R.; Setzler, B. P.; Lin. S.; Wang, J.;
672		Zhao, Y.; Xu, H.; Pivovar, B.; Tian, B.; Chen, X.; Wu, G.; Yan, Y. A Roadmap to low-
673		cost hydrogen with hydroxide exchange membrane electrolyzers. Adv. Mater. 2019, 31,
674		1805876. (j) Vincent, I.; Bessarabov, D. Low-cost hydrogen production by anion
675		exchange membrane electrolysis: A review. Renew. Sustain. Energy Rev. 2018, 81,
676		1690–1704.
677	4.	(a) Huang, A. M.; Su, A.; Liu, Y. C. Hydrogen generator system using Ru catalyst for
678		PEMFC (proton exchange membrane fuel cell) applications. Energy 2013, 51, 230-
679		236. (b) Kim, J.; Kim, T. Compact PEM fuel cell system combined with all-in-one
680		hydrogen generator using chemical hydride as a hydrogen source. Appl. Energy 2015,
681		160, 945–953. (c) Kim, K.; Kim, T.; Lee K.; Kwon, S. Fuel cell system with sodium
682		borohydride as hydrogen source for unmanned aerial vehicles. J. Power Sources 2011,
683		196, 9069–9075.
684	5.	(a) Ren. J.; Musyoka, N. N.; Langmi, H.W.; Mathe, M.; Liao, S. Current research trends
685		and perspectives on materials-based hydrogen storage solutions: A critical review. Int.

- *J. Hydrogen Energy* 2017, *42*, 289–311. (b) Rivard, E.; Trudeau, M.; Zaghib, K.
 Hydrogen Storage for Mobility: A Review. *Materials* 2019, *12*, 1973.
- 6. (a) Demirci, U. B.; Miele, P. Chemical hydrogen storage: 'material' gravimetric
 capacity versus 'system' gravimetric capacity. *Energy Environ. Sci.* 2011, *4*, 3334–
 3341. (b) Schneemann. A.; White, J. L.; Kang, S. Y.; *et al.* Nanostructured Metal

Hydrides for Hydrogen Storage. *Chem. Rev.* 2018, *118*, 10755–10839. (c) Yu X.; Tang
Z.; Sun D.; Ouyang, L.; Zhu, M. Recent advances and remaining challenges of
nanostructured materials for hydrogen storage applications. *Progress Mater. Sci.* 2017, *88*, 1-48. (e) Eberle, U.; Felderhoff, M.; Schueth, F. Chemical and physical solutions
for hydrogen storage. *Angew. Chem. Int. Ed.* 2009, *48*, 6608–6630.

- 7. (a) Lang, C.; Jia, Y.; Yao, X. Recent advances in liquid-phase chemical hydrogen 696 697 storage. Energy Storage Mater. 2020, 26, 290-312. (b) Wang, C.; Wang, Q.; Fu, F.; Astruc, D. Hydrogen generation upon nanocatalyzed hydrolysis of hydrogen-rich boron 698 699 derivatives: recent developments. Acc. Chem. Res. 2020, 53, 2483-2493. (c) Sun, Q.; Wang, N.; Xu, Q.; Yu, J. Nanopore-supported metal nanocatalysts for efficient 700 hydrogen generation from liquid-phase chemical hydrogen storage materials. Adv. 701 702 Mater. 2020, 32, 2001818. (d) Wang, C.; Astruc, D. Recent developments of nanocatalyzed liquid-phase hydrogen generation. Chem. Soc. Rev. 2021, 50, 3437-84. 703 (e) Staubitz, A.; Robertson, A. P. M.; Manners, I. Ammonia-Borane and Related 704 Compounds as Dihydrogen Sources. Chem. Rev. 2010, 110, 4079-124. (f) Hamilton, 705 C. W.; Baker, R. T.; Staubitz, A.; Manners, I. B-N compounds for chemical hydrogen 706 storage. Chem. Soc. Rev. 2009, 38, 279-93. (g) Yadav, M.; Xu, Q. Liquid-phase 707 chemical hydrogen storage materials. Energy Mater. Sci. 2012, 5, 9698-725. (h) Zhu, 708 709 Y.; Ouyang, L.; Zhong, H.; Liu, J.; Wang, H.; Shao, H.; Huang, Z.; Zhu, M. Angew. 710 Chem. Int. Ed. 2020, 59, 8623-8629.
- 8. (a) Abdelhamid H. N. A review on hydrogen generation from the hydrolysis of sodium
 borohydride. *Int. J. Hydrogen Energy* 2021, *46*, 726–765. (b) Muir, S. S., Yao, X.
 Progress in sodium borohydride as a hydrogen storage material: Development of
 hydrolysis catalysts and reaction systems. *Int. J. Hydrogen Energy* 2011, *36*, 5983–
 5997. (c) Santos, D. M. F.; Sequeira, C. A. C. Sodium borohydride as a fuel for the

future. *Rev. Sustain. Energy Rev.* 2011, *15*, 3980–4001. (d) Liu, B. H.; Li, Z. P. A review:
Hydrogen generation from borohydride hydrolysis reaction. *J. Power Sources* 2009, *187*, 527–34. (e) Zhu, Y.; Ouyang, L.; Zhong, H.; Liu, J.; Wang, H.; Shao, H.; Huang,
Z.; Zhu, M. Closing the Loop for Hydrogen Storage: Facile Regeneration of NaBH4
from its Hydrolytic Product. *Angew. Chem. Int. Ed.* 2020, *59*, 8623-8629.

- 9. (a) Brack, P.; Dann, S. E.; Wijayantha, K. G. U. Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride
 (NaBH₄) solutions. *Energy Sci. Eng.* 2015, *3*, 17–88. (b) Dragan, M. Hydrogen Storage
 in Complex Metal Hydrides NaBH₄: Hydrolysis Reaction and Experimental Strategies. *Catalysts* 2022, *12*, 356.
- 10. (a) Sordakis, K.; Tang, C.; Vogt, L. K.; Junge, H.; Dyson, P. J.; Beller, M.; Laurenczy, 726 727 G. Homogeneous catalysis for sustainable hydrogen storage in formic acid and alcohols. Chem. Rev. 2017, 118, 372-433. (b) Onishi, N.; Laurenczy, G.; Beller, M.; 728 Himeda, Y. Recent progress for reversible homogeneous catalytic hydrogen storage in 729 730 formic acid and in methanol. Coord. Chem. Rev. 2018, 373, 317-332. (c) Hamilton, C. W.; Baker, R. T.; Staubitz, A.; Manners, I. B-N compounds for chemical hydrogen 731 storage. Chem. Soc. Rev. 2009, 38, 279-293. (d) Onishi, N.; Iguchi, M.; Yang, X.; 732 Kanega, R.; Kawanami, H.; Xu, Q.; Himeda, Y. Development of effective catalysts for 733 734 hydrogen storage technology using formic acid. Adv. Energy Mater. 2009, 9, 1801275. 735 (e) Shimbayashi, T.; Fujita, K. Metal-catalyzed hydrogenation, and dehydrogenation reactions for efficient hydrogen storage. Tetrahedron 2020, 76, 130946. 736 11. (a) Luconi, L.; Tuci, G.; Giambastiani, G.; Rossin, A.; Peruzzini, M. H₂ production from 737
- lightweight inorganic hydrides catalyzed by 3d transition metals. *Int. J. Hydrogen Storage* 2019, 44, 25746–25776. (b) Li, Z.; Xu, Q. Metal-nanoparticle-Catalyzed
 Hydrogen generation from formic. *Acc. Chem. Res.* 2017, *50*, 1449–1458. (c) Zhan, W.

W.; Zhu, Q. L.; Xu, Q. Dehydrogenation of ammonia borane by metal nanoparticle
catalysts. *ACS Catal.* 2016, *6*, 6892–6905. (d) Wang, C.; Astruc, D. Recent
developments of nanocatalyzed liquid-phase hydrogen generation. *Chem. Soc. Rev.*2021, *50*, 3437–3484. (e) Patel, N.; Miotello, A. Progress in Co–B related catalyst for
hydrogen production by hydrolysis of boron-hydrides: A review and the perspectives to
substitute noble metals. *Int. J. Hydrogen Energy* 2015, 40, 1429–1464.

12. (a) Yang, X. F.; Wang, A.; Qiao, B.; Li, J.; Liu, J.; Zhang, T. Single-atom catalysts: A
new frontier in heterogeneous catalysis. *Acc. Chem. Res.* 2013, *46*, 1740–1748. (b)
Schmid, G. Nanoparticles: From theory to applications, Wiley-VCH, Weinheim, 2004,
1–359.

13. (a) Li, X. T.; Zhang, X. L.; Peng, Z. K.; Liu, P.; Zheng, X. C. Hierarchical porous g-751 752 C₃N₄ coupled ultrafine RuNi alloys as extremely active catalysts for the hydrolytic dehydrogenation of ammonia borane. ACS Sustainable Chem. Eng. 2020, 8, 8458-753 8468. (b) Li, X.; Zhang, C.; Luo, M.; Yao, Q.; Lu, Z. H. Ultrafine Rh nanoparticles 754 confined by nitrogen-rich covalent organic frameworks for methanolysis of ammonia 755 borane. Inorg. Chem. Front. 2020, 7, 1298–1306. (c) Ding, R.; Chen, Q.; Luo, Q.; Zhou, 756 L.; Wang, Y.; Zhang, Y.; Fan, G. Salt template-assisted in situ construction of Ru 757 nanoclusters and porous carbon: excellent catalysts toward hydrogen evolution, 758 ammonia-borane hydrolysis, and 4-nitrophenol reduction. Green Chem. 2020, 22, 835-759 760 842. (d) Yin, L.; Zhang, T.; Dai, K.; Zhang, B.; Xiang, X.; Shang, H. Ultrafine PtCo alloy nanoclusters confined in N-doped mesoporous carbon spheres for efficient 761 ammonia borane Hydrolysis. ACS Sustainable Chem. Eng. 2021, 9, 822-832. (e) 762 763 Biehler, E.; Quach Q.; Abdel-Fattah T. M. Application of Palladium Mesoporous Carbon Composite Obtained from a Sustainable Source for Catalyzing Hydrogen 764 Generation Reaction. J. Compos. Sci. 2024, 8, 270. (f) Huff, C.; Long, J. M.; Heyman, 765

- A.; Abdel-Fattah, T. M. ACS Appl. Energy Materials 2018, 1, 4635–4640. (g)
 Uzundurukan, A.; Devrim, Y. Hydrogen generation from sodium borohydride
 hydrolysis by multi-walled carbon nanotube supported platinum catalyst: A kinetic
 study. Int. J. Hydrogen Energy 2019, 44, 17586–17594.
- 14. (a) Sun, Q.; Wang, N.; Bing, Q.; Si, R.; Liu, J.; Bai, R.; Zhang, P.; Jia, M.; Yu, J. 770 Subnanometric hybrid Pd-M(OH)₂, M = Ni, Co, clusters in zeolites as highly efficient 771 772 nanocatalysts for hydrogen generation. Chem. 2017, 3, 477-493. (b) Wang, N.; Sun, Q.; Bai, R.; Li, X.; Guo, G.; Yu, J. In situ confinement of ultrasmall Pd clusters within 773 774 nanosized silicalite-1 zeolite for highly efficient catalysis of hydrogen generation. J. Am. Chem. Soc. 2016, 138, 7484–7487. (c) Sun, Q.; Wang, N.; Zhang, T. R.; Mayoral, 775 A.; Zhang, P.; Zhang, Q.; Terasaki, O.; Yu, J. Zeolite-encaged single-atom rhodium 776 catalysts: highly efficient hydrogen generation and shape-selective tandem 777 hydrogenation of nitroarenes. Angew. Chem. Int. Ed. 2019, 58, 18570-18576. (d) 778 Zahmakiran, M.; Özkar, S. Zeolite-Confined Ruthenium(0) nanoclusters catalyst: 779 record catalytic activity, reusability, and lifetime in hydrogen generation from the 780 hydrolysis of sodium borohydride. Langmuir 2009, 25, 2667-2678. (e) Sun, Q.; Wang, 781 N.; Bai, R.; Hui, Y.; Zhang, T.; Do, D. A.; Zhang, P.; Song, L.; Miao, S.; Yu, J. 782 Synergetic effect of ultrasmall metal clusters and zeolites promoting hydrogen 783 generation. Adv. Sci. 2019, 6, 1802350. (f) Zahmakiran, M.; Ayvali, T.; Akbayrak, S.; 784 Caliskan, S.; Celik, D.; Özkar, S. Zeolite framework stabilized nickel(0) nanoparticles: 785 Active and long-lived catalyst for hydrogen generation from the hydrolysis of 786 ammonia-borane and sodium borohydride. Catal. Today 2011, 170, 76-84. 787 788 15. (a) Altaf, C. T.; Minkina, V. G.; Shabunya, S. I.; Colak, T. O.; Sankir, N. D.; Sankir,
- M.; Kalinin. V. I. Ruthenium and Platinum-Modified Titanium Dioxide Support for
 NaBH₄ Hydrolysis. *ACS Omega* 2023, *8*, 36100–36108. (b) Li, T.; Xiang, C.; Chu, H.;

Xu, F.; Sun, L.; Zou, Y.; Zhang, J. Catalytic effect of highly dispersed ultrafine Ru 791 nanoparticles on a TiO₂-Ti₃C₂ support: Hydrolysis of sodium borohydride for H₂ 792 generation. J. Alloys Compd. 2022, 906, 164380. (c) Altaf, C. T.; Colak, T. O.; Minkina, 793 V. G.; Shabunya, S. I.; Sankir, M.; Sankir, N. D.; Kalinin, V. I. Effect of Titanium 794 Dioxide Support for Cobalt Nanoparticle Catalysts for Hydrogen Generation from 795 Sodium Borohydride Hydrolysis. Catal. Lett. 2022, 153 (10), 3136-3147. (d) Kılınç, 796 797 D.; Şahin, O. Effective TiO₂ supported Cu-Complex catalyst in NaBH₄ hydrolysis reaction to hydrogen generation. Int. J. Hydrogen Energy 2019, 44 (34), 18858-18865. 798 799 (e) Tanyildizi, S.; Morkan, İ.; Özkar, S. Nanotitania-supported Rhodium(0) nanoparticles: superb catalyst in dehydrogenation of dimethylamine borane. Chem. 800 Select 2017, 2, 5751-5759. (f) Karaboga, S.; Özkar, S. Nanoalumina supported 801 802 palladium (0) nanoparticle catalyst for releasing H₂ from dimethylamine borane. Appl. Surf. Sci. 2019, 487, 433–441. (g) Mori, K.; Taga, T.; Yamashita, H. Synthesis of a Fe-803 Ni alloy on a ceria support as a noble-metal-free catalyst for hydrogen production from 804 chemical hydrogen storage materials. ChemCatChem 2015, 7, 1285-1291. (h) Bozkurt, 805 G.; Ozer, A.; Yurtcan, A. B. Development of effective catalysts for hydrogen generation 806 from sodium borohydride: Ru, Pt, Pd nanoparticles supported on Co₃O₄, *Energy* 2019, 807 180, 702–713. 808

16. (a) Verma, P.; Yuan, K.; Kuwahara, Y.; Moria, K.; Yamashita, H. Enhancement of plasmonic activity by Pt/Ag bimetallic nanocatalyst supported on mesoporous silica in the hydrogen production from hydrogen storage material. *Appl. Catal. B* 2018, *223*, 10–15. (b) Patel, N.; Fernandes, R.; Gupta, S.; Edla, R.; Kothari, D. C.; Miotello, A. Co-B catalyst supported over mesoporous silica for hydrogen production by catalytic hydrolysis of ammonia borane: A study on influence of pore structure. *Appl. Catal. B* 2013, *140-141*, 125–132. (c) Mori, K.; Futamura, Y.; Masuda, S.; Kobayashi, H.;

Yamashita, H. Controlled release of hydrogen isotope compounds and tunnelling effect
in the heterogeneously catalyzed formic acid dehydrogenation. *Nat. Commun.* 2019, *10*, 4094.

- 819 17. (a) Zhong, H.; Su, Y.; Cui, C.; Zhou, F.; Li, X.; Wang, R. Palladium Nanoparticles
 820 supported by carboxylate-functionalized porous organic polymers for additive-free
 821 hydrogen generation from formic acid. *ACS Sustainable Chem. Eng.* 2017, *5*, 8061–
 822 8069. (b) Cui, C.; Tang, Y.; Ziaee, M. A.; Tian, D.; Wang, R. Highly Dispersed Ultrafine
 823 Palladium nanoparticles enabled by functionalized porous organic polymer for
 824 additive-free dehydrogenation of formic acid. *ChemCatChem* 2018, *10*, 1431–1437.
- 18. (a) Wang, H.; Xu, F.; Sun, L.; Wu, J.; Zhang, G.; Zhu, Y.; Shao, Q.; Luo, Y.; Peng, 825 Wang, Y.; Gao, Y.; Zou, Y. Novel MOF/COF dual carrier anchoring Ru nanoparticles 826 827 for improved hydrogen production by hydrolysis of NaBH₄. J. Alloys Compd. 2024, 978, 173415. (b) Song, F. Z.; Zhu, Q. L.; Yang, X.; Zhan, W. W.; Pachfule, P.; Tsumori, 828 N.; Xu, Q. Metal-organic framework templated porous carbon-metal oxide/reduced 829 graphene oxide as superior support of bimetallic nanoparticles for efficient hydrogen 830 generation from formic acid. Adv. Energy Mater. 2018, 8, 1701416. (c) Zhu, B.; Zou, 831 R.; Xu, Q. Metal-organic framework-based catalysts for hydrogen evolution. Adv. 832 Energy Mater. 2018, 8, 1801193. (d) Tuan, D. D.; Lin, K.-Y. A. Ruthenium supported 833 on ZIF-67 as an enhanced catalyst for hydrogen generation from hydrolysis of sodium 834
- borohydride. *Chem. Eng. J.* **2018**, *351*, 48–55.
- 19. (a) Kang, N.; Djeda, R.; Wang, Q.; Fu, F.; Ruiz, J.; Pozzo, J. L.; Astruc, D. Efficient
 "Click"-Dendrimer-supported synergistic bimetallic nanocatalysis for hydrogen
 evolution by sodium borohydride hydrolysis. *ChemCatChem* 2019, *11*, 2341–2349. (b)
 Wang, Q.; Fu, F.; Escobar, A.; Moya, S.; Ruiz, J.; Astruc, D. Click" Dendrimerstabilized nanocatalysts for efficient hydrogen release upon ammonia-borane

- hydrolysis. *ChemCatChem* 2018, *10*, 2673–2680. (c) Wang, Q.; Fu, F.; Yang, S.; Moro,
 M. M.; de los Angeles Ramirez, M.; Moya, S.; Salmon, L.; Ruiz, J.; Astruc, D. Dramatic
 synergy in CoPt nanocatalysts stabilized by "click" dendrimers for evolution of
 hydrogen from hydrolysis of ammonia borane. *ACS Catal.* 2019, *9*, 1110–1119.
- 20. Rakap, M. Hydrolysis of Sodium Borohydride and Ammonia Borane for Hydrogen
 Generation Using Highly Efficient Poly(N-Vinyl-2-Pyrrolidone)-Stabilized Ru–Pd
 Nanoparticles as Catalysts. *Int. J. Green Energy* 2015, *12*, 1288–1300.
- 21. (a) Lu, L.; Zou, S.; Fang, B. The critical impacts of ligands on heterogeneous 848 849 nanocatalysis: A review. ACS Catal. 2021, 11, 6020-6058. (b) Rossi, L. M.; Fiorio, J. L.; Garcia, M. A. S.; Ferraz, C. P. The role and fate of capping ligands in colloidally 850 prepared metal nanoparticle catalysts. Dalton Trans. 2018, 47, 5889-5915 126. (c) 851 Campisi, S.; Schiavoni, M.; Chan-Thaw C. E.; Villa, A. Untangling the role of the 852 capping agent in nanocatalysis: recent advances and perspectives. Catalysts 2016, 6, 853 185. (d) Liu, K.; Qin, R.; Zheng, N. Insights into the interfacial effects in heterogeneous 854 metal nanocatalysts toward selective hydrogenation. J. Am. Chem. Soc. 2021, 143, 855 4483-4499. 856
- 22. (a) Doherty, S.; Knight J. G.; Backhouse, T. et al. Highly efficient aqueous phase 857 chemoselective hydrogenation of α , β -unsaturated aldehydes catalysed by phosphine-858 decorated polymer immobilized IL-stabilized PdNPs. Green Chem. 2017, 19, 1635-859 1641. (b) Doherty, S.; Knight, J. G.; Backhouse, T. et. al. Highly efficient aqueous 860 phase reduction of nitroarenes catalyzed by phosphine-decorated polymer immobilized 861 ionic liquid stabilized PdNPs. Catal. Sci. Technol. 2018, 8, 1454-1467. (c) Doherty, S.; 862 Knight, J. G.; Backhouse, T. et. al. Heteroatom Donor-Decorated Polymer-Immobilized 863 Ionic Liquid Stabilized Palladium Nanoparticles: Efficient Catalysts for Room-864 Temperature Suzuki-Miyaura Cross-Coupling in Aqueous Media. Adv. Synth. Catal. 865

2018, 360, 3716–3731. (d) Doherty, S.; Knight, J. G.; Backhouse, T. et al. Highly 866 efficient and selective aqueous phase hydrogenation of aryl ketones, aldehydes, furfural 867 and levulinic acid and its ethyl ester catalyzed by phosphine oxide-decorated polymer 868 immobilized ionic liquid-stabilized ruthenium nanoparticles. Catal. Sci. Technol. 2022, 869 12, 3549-67. (e) Doherty, S.; Knight, J. G.; Backhouse, T. et al. Highly Selective and 870 Reduction of Nitrobenzene to N-Phenylhydroxylamine, 871 Solvent-Dependent 872 Azoxybenzene, and Aniline Catalyzed by Phosphino-Modified Polymer Immobilized Ionic Liquid-Stabilized AuNPs. ACS Catal. 2019, 9, 4777-91. (f) Doherty, S.; Knight 873 874 J. G.; Paterson, R. et al. Highly efficient and selective partial reduction of nitroarenes N-arylhydroxylamines catalysed by phosphine oxide-decorated polymer 875 to immobilized ionic liquid stabilized ruthenium nanoparticles. J. Catal. 2023, 417, 74-876 88. (g) Paterson, R.; Fahy, L. F.; Arca, E.; Dixon, C.; Wills, C.; Yan, H.; Griffiths, A.; 877 Collins, S. M.; Wu, K. J.; Bourne, R. A.; Chamberlain, T. W.; Knight, J. G.; Doherty, S. 878 Amine-modified polyionic liquid supports enhance the efficacy of PdNPs for the 879 catalytic hydrogenation of CO₂ to formate. Chem. Commun. 2023, 59, 13470-13473. 880 (h) Doherty, S.; Knight, J. G.; Paterson, R. et al. Heteroatom Modified Polymer 881 Immobilized Ionic Liquid Stabilized Ruthenium Nanoparticles: Efficient Catalysts for 882 the Hydrolytic Evolution of Hydrogen from Sodium Borohydride. Mol. Catal. 2022, 883 528, 112476. (i) Alharbi A. A.; Wills C.; Chamberlain, T. W.; Bourne R. A.; Griffiths 884 A.; Collins S. M.; Wu, K. J.; Mueller, P, Knight, J. G.; Doherty, S. Amino-Modified 885 Polymer Immobilized Ionic Liquid Stabilized Ruthenium Nanoparticles: Efficient and 886 Selective Catalysts for the Partial and Complete Reduction of Quinolines. 887 ChemCatChem 2023, 15, e202300418. 888

23. (a) F. Giacalone, F.; M. Gruttadauria M. Covalently Supported Ionic Liquid Phases: An
Advanced Class of Recyclable Catalytic Systems. *ChemCatChem* 2016, *8*, 664–684.

(b) Bordet, A.; Leitner, W. Metal Nanoparticles Immobilized on Molecularly Modified 891 Versatile Catalytic Systems for Controlled Hydrogenation 892 Surfaces: and Hydrogenolysis. Acc. Chem. Res. 2021, 54, 2144-2157. (c) Zhu, M.; Yanga, Y. 893 Poly(ionic liquid)s: an emerging platform for green chemistry. Green Chem. 2024, 26, 894 5022-5102. (d) Li, H.; Pinaki, S. Bhadury, P. S.; Song, B.; Yang, S. Immobilized 895 functional ionic liquids: efficient, green, and reusable catalysts. RSC Adv. 2012, 2, 896 897 12525–12551. (e) Zhu, M. Ionic-liquid/metal-organic-framework composites: synthesis and emerging sustainable applications. Inorg. Chem. Front. 2025, 12, 39-84. 898 899 24. (a) Anandaraj, S. J. L.; Kang, L.; DeBeerm S.; Bordet, A.; Leitner, W. Catalytic Hydrogenation of CO₂ to Formate Using Ruthenium Nanoparticles Immobilized on 900 Supported Ionic Liquid Phases. Small 2023, 19, 2206806. (b) Feng, B.; Zhang, Z.; 901 902 Wang, J.; Yang, D.; Li, Q.; Liu, Y.; Gai, H.; Huang, T.; Song, H. Synthesis of hydrophobic Pd-poly(ionic liquid)s with excellent CO₂ affinity to efficiently catalyze 903 CO₂ hydrogenation to formic acid. Fuel 2022, 325, 124853. (c) Li, Q.; Huang, T.; 904 Zhang, Z.; Xiao, M.; Gai, H.; Zhou, Y.; Song, H. Highly Efficient Hydrogenation of 905 CO2 to Formic Acid over Palladium Supported on Dication Poly(ionic liquid)s. Mol. 906 Catal. 2021, 509, 111644. 907

25. (a) Cavia, C.; Ballerini, E.; Bivona, L. A.; Giacalone, F.; Aprile, C.; Vaccaro, L.; 908 Gruttadauria, M. Palladium Supported on Cross-Linked Imidazolium Network on 909 910 Silica as Highly Sustainable Catalysts for the Suzuki Reaction under Flow Conditions. Adv. Synth. Catal. 2013, 355, 2007–2018. (b) Pavia, C.; Giacalone, F.; Bivona, L. A.; 911 Vaccaro, L.; Aprile, C.; Pia Salvo, A. M.; Petrucci, C.; Strappaveccia, G.; 912 Gruttadauria M. Evidences of release and catch mechanism in the Heck reaction 913 catalyzed by palladium immobilized on highly cross-linked-supported imidazolium 914 salts. J. Mol. Cat. A 2014, 4, 387, 57-62. (c) Karimi, B.; Mansouri, F.; Vali, H. A highly 915

water-dispersible/magnetically separable palladium catalyst based on a Fe₃O₄@SiO₂
anchored TEG-imidazolium ionic liquid for the Suzuki–Miyaura coupling reaction in
water. *Green Chem.* 2014, *16*, 2587–2596.

- 26. Restrepo, J.; Porcar, R.; Lozano, P.; Butguete, M. I.; Garcia-Verdugo, E.; Luis, S. V.
 Microwave-Assisted Selective Oxidation of 1-Phenyl Ethanol in Water Catalyzed by
 Metal Nanoparticles Immobilized onto Supported Ionic Liquidlike Phases. *ACS Catal.*2015, 5, 4743–4750.
- 27. (a) Zhang, Z.; Gai, H.; Li, Q.; Feng, B.; Xiao, M.; Huang, T.; Song, H. Effect anions on 923 924 the hydrogenation of nitrobenzene over N-rich Poly(ionic liquid) supported Pd catalyst. Chem. Eng. J. 2022, 429, 132224. (b) Lei, Y.; Chen, Z.; Lan, G.; Ang, R.; Zhou, X.-Y. 925 Pd nanoparticles stabilized with phosphine-functionalized porous ionic polymer for 926 927 efficient catalytic hydrogenation of nitroarenes in water. N. J. Chem. 2020, 44, 3681-3689. (c) H. Song, H.; Y. Liu, Y.; Y. Wang, Y.; B. Feng, B.; X. Jin, X.; T. Huang, T.; M. 928 Xiao, M.; H. Gai, H. Design of hypercrosslinked poly(ionic liquid)s for efficiently 929 catalyzing high-selective hydrogenation of phenylacetylene under ambient conditions. 930 Mol. Catal. 2020, 493, 111081. (d) Montolio, S.; Vicent, C.; Aseyev, V.; Alfonso, I.; 931 Burguete, M. I.; Tenhu, H.; García-Verdugo, E.; Luis, S. V. AuNP-Polymeric Ionic 932 Liquid Composite Multicatalytic Nanoreactors for One-Pot Cascade Reactions. ACS 933 Catal. 2016, 6, 7230V7237. 934
- 28. (a) Ziaee, M. A.; Zhong, H.; Cui, C.; Wang, R. Additive Free hydrogen Generation from
 Formic Acid Boosted by Amine-Functionalized Imidazolium-Based Ionic Polymers. *ACS Sus. Chem. Eng.* 2018, *6*, 10421–2387. (b) Ziaee, M. A.; Tang, Y.; Zhong, H.; Tian,
 D.; Wang, R. Urea-Functionalized Imidazolium-Based Ionic Polymer for Chemical
 Conversion of CO₂ into Organic Carbonates. *ACS Sus. Chem. Eng.* 2018, *6*, 2380–2387.

- 940 29. Gong, Y.; Zhong, H.; Liu, W.; Zhang, B.; Hu, S.; Wang, R. General Synthetic Route
 941 toward Highly Dispersed Ultrafine Pd–AuAlloy Nanoparticles Enabled by
 942 Imidazolium-Based Organic Polymers. *ACS Appl. Mater. Interfaces* 2018, 10,
 943 776–786.
- 30. Al-shaikh, H.; Lasri, J.; Knight, J. G.; Al-Gou, S. T. Palladium mesoporous
 nanoparticles Pd NPs@[KIT-6] and Pd NPs@[KIT-6]-PEG-imid as efficient
 heterogeneous catalysts for H₂ production from NaBH₄ hydrolysis. *Fuel* 2022, *325*,
 124964.
- 31. (a) Saptal, V. B.; Sasaki, T.; Bhanage, B. M. Ru@PsIL-catalyzed synthesis of Nformamides and benzimidazole by using carbon dioxide and dimethylamine borane. *ChemCatChem* 2018, 10, 2593–2600. (b) Patil, M. N.; Sasaki, T.; Bhanage, B. M.;
 Immobilized ruthenium metal-containing ionic liquid-catalyzed dehydrogenation of
 dimethylamine borane complex for the reduction of olefins and nitroarenes. *RSC Adv.*2016, 6, 52347–52352.
- 32. (a) Alharbi, A. A.; Wills, C.; Dixon, C.; Arca, E.; Chamberlain, T. W.; Griffiths, 954 A.; Collins, S. M.; Wu, K.; Yan, H.; Bourne, R. A.; Knight, J. G.; Doherty S. Efficient 955 Hydrogen Evolution from Dimethylamine Borane, Ammonia Borane and Sodium 956 Borohydride Catalyzed by Ruthenium and Platinum Nanoparticles Stabilized by an 957 Amine Modified Polymer Immobilized Ionic Liquid: A Comparative Study. Catal. Lett. 958 2024, 154, 5450-5471. (b) Doherty, S.; Knight, J. G.; Alharbi, H.; Paterson, R.; Wills, 959 C.; Dixon, C.; Šiller, L; Chamberlain. T. W.; Griffiths, A.; Collins, S. M.; Wu, K. J.; 960 Simmons, M. D.; Bourne, R. A.; Lovelock, K. R. J.; Seymour, J. Efficient hydrolytic 961 hydrogen evolution from sodium borohydride catalyzed by polymer immobilized ionic 962 liquid-stabilized platinum nanoparticles. ChemCatChem 2022, 14, e202101752. 963

33. (a) Zhang, S.; Zhou, L.; Chen, M. Amine-functionalized MIL-53(Al) with embedded 964 ruthenium nanoparticles as a highly efficient catalyst for the hydrolytic 965 dehydrogenation of ammonia borane. RSC Adv. 2018, 8, 12282–12291. (b) Wang, Z.; 966 Zhang, H.; Chen, L.; Miao, S.; Wu, S.; Hao, X.; Zhang, W.; Jia, M. Interfacial Synergy 967 of PtPd Nanoparticles Dispersed on Amine-Modified ZrSBA-15 in Catalytic 968 Dehydrogenation of Ammonia Borane and Reduction of p-Nitrophenol. J. Phys. Chem. 969 970 C 2018, 122, 12975–12983. (c) Zhao, L.; Wei, Q.; Zhang, L.; Zhao, Y.; Zhang, B. NiCo alloy decorated on porous N-doped carbon derived from ZnCo-ZIF as highly efficient 971 972 and magnetically recyclable catalyst for hydrogen evolution from ammonia borane. Renew. Energy 2021, 173, 273–282. 973 34. (a) Bulushev, D. A.; Zacharska, M.; E. Shlyakhova, E. V.; Chuvilin, A. L.; Guo, Y.; 974 Beloshapkin, S.; Okotrub, A. V.; Bulusheva, L. G. Single Isolated Pd2+ Cations 975 Supported on N-Doped Carbon as Active Sites for Hydrogen Production from Formic 976 Acid Decomposition. ACS Catal. 2016, 6, 681–691. (b) Li, Z.; Yu, H.; Zhang, Y.; Wu, 977 D.; Bai, Y.; Liu, S.; Zhao, H. An attempt to confirm the contribution to ORR activity of 978 different N-species in M-NC (M = Fe, Co, Ni) catalysts with XPS analysis. Chem. 979 Commun. 2023, 59, 4535–4538. (c) Chatterjee, P.; Wang, H.; Manzano, J. S.; Kanbur, 980 U.; Sadow, A. D.; Slowing, I. I. Surface ligands enhance the catalytic activity of 981 supported Au nanoparticles for the aerobic α -oxidation of amines to amides. *Catal. Sci.* 982 Technol. 2022, 12, 1922–1933. (d) Militello, M. C.; Simko, S. J. Palladium Chloride 983 (PdCl₂) by XPS. Surf. Sci. Spectra 1994, 3, 402–409. (e) He, Z.; Dong, B.; Wang, W.; 984 Yang, G.; Cao, Y.; Wang, H.; Yang, Y.; Wang, Q.; Peng, F.; Yu, H. Elucidating 985 Interaction between Palladium and N-Doped Carbon Nanotubes: Effect of Electronic 986 Property on Activity for Nitrobenzene Hydrogenation. ACS Catal. 2019, 9, 2893–2901. 987 (f) Cristau, H.-J.; Hervé, A.; Loiseau, F.; Virieux, D. Synthesis of New 988

- 989 Arylhydroxymethylphosphinic Acids and Derivatives. *Synth.* **2003**, *14*, 2216–2220. (g)
- 990 Arrigo, R.; Schuster, M. E.; Abate, S.; Wrabetz, S.; Amakawa, K.; Teschner, D.; Freni,
- 991 M.; Centi, G.; Perathoner, S.; Havecker, M.; Schlögl, R. ChemSusChem, 2014, 7, 179–
- 992 194. (h) Zemlyanov, D.; Aszalos-Kiss, B.; Kleimenov, E.; Teschner, D.; Zafeiratos, S.;
- Hävecker, M.; Knop-Gericke, A.; Schlögl, R.; Gabasch, H.; Unterberger, W.; Hayek,
 K.; Klötzer, B. *Surf. Sci.*, 2006, 600, 983–994.
- 35. (a) Koh, K.; Seo, J.-E.; Lee, J. H.; Goswami, A.; Yoon, C. W.; Asefa, T. Ultrasmall
 palladium nanoparticles supported on amine-functionalized SBA-15 efficiently
 catalyze hydrogen evolution from formic acid. *J. Mater. Chem. A* 2014, *2*, 20444–
 20449. (b) Koh, K.; Jeon, M.; Yoon, C. W.; Asefa, T. Formic acid dehydrogenation over
 Pd NPs supported on amine-functionalized SBA-15 catalysts: structure-activity
 relationships. *J. Mater. Chem. A* 2017, *5*, 16150–16161.
- 36. (a) Shao, X.; Miao, X.; Yu, X.; Wang W.; Ji, X. Efficient synthesis of highly dispersed
 ultrafine Pd nanoparticles on a porous organic polymer for hydrogenation of CO₂ to
 formate. *RSC Adv.* 2020, 10, 9414–9419. (b) Shi, G.; Dong, Z. Palladium Supported on
 Porous Organic Polymer as Heterogeneous and Recyclable Catalyst for Cross Coupling
 Reaction. *Molecules* 2022, *27* (15), 4777.
- 37. Jiang, S.; Liu, X.; Zhai, S.; Ci, X.; Yu, T.; Sun, L.; Zhai, D.; Deng W.; Ren G. Additivefree CO₂ hydrogenation to pure formic acid solution via amine-modified Pd catalyst at
 room temperature. *Green Chem.* 2023, *25*, 6025–6031.
- 38. Ding, Y.; Sun, X.; Peng, W.-F.; Zhang, L.; Meng, S.; Yao, Q.; Feng, G.; Lu, Z.-H. Fast
 and Durable Dehydrogenation of Formic Acid over Pd–Cr(OH)₃ Nanoclusters
 Immobilized on Amino-Modified Reduced Graphene Oxide. *Ind. Eng. Chem. Res.*2023, 62, 6963–6972.

- 1013 39. (a) Jin, M-H.; Park, J.-H.; Oh, D.; Park, J.-S.; Lee, K.-Y.; Lee, D.-W. Effect of the amine group content on catalytic activity and stability of mesoporous silica supported Pd 1014 catalysts for additive-free formic acid dehydrogenation at room temperature. Int. J. 1015 Hydrogen Energy 2019, 44, 4737–4744. (b) Jin, M-H.; Park, J.-H.; Oh, D.; Lee, S.-W.; 1016 Park, J.-S.; Lee, K. Y.; Lee, D.-W. Pd/NH₂-KIE-6 catalysts with exceptional catalytic 1017 activity for additive-free formic acid dehydrogenation at room temperature: Controlling 1018 1019 Pd nanoparticle size by stirring time and types of Pd precursors. *Int. J. Hydrogen Energy* **2018**, *43*, 1451–1458. 1020
- 1021 40. (a) Jeon, M.; Han, D. J.; Lee, K.-S.; Choi, S. H.; Han, J.; Nam, S. W.; Jang, C. S.; Park,
- 1022 H. S.; Yoon, C. W. Electronically modified Pd catalysts supported on N-doped carbon
- 1023 for the dehydrogenation of formic acid. Int. J. Hydrogen Energy 2016, 41, 15453-
- 1024 15461. (b) He Z.; Dong, B.; Wang, W.; Yang, G.; Cao, Y.; Wang, H.; Yang, Y.; Wang,
- Q.; Peng, F.; Yu H. Elucidating Interaction between Palladium and N-Doped Carbon
 Nanotubes: Effect of Electronic Property on Activity for Nitrobenzene Hydrogenation.
 ACS Catal. 2019, *9*, 2893–2901.
- 41. Song, F.-Z.; Zhu, Q.-L.; Tsumori, N.; Xu, Q. Diamine-Alkalized Reduced Graphene
 Oxide: Immobilization of Sub-2 nm Palladium Nanoparticles and Optimization of
 Catalytic Activity for Dehydrogenation of Formic Acid. *ACS Catal.* 2015, *5*, 5141–
 5144.
- 1032 42. Biehler, E.; Quach, Q. Clay Huff and Tarek M. Abdel-Fattah, Organo-Nanocups Assist
 1033 the Formation of Ultra-Small Palladium Nanoparticle Catalysts for Hydrogen
 1034 Evolution Reaction. *Materials* 2022, *15*, 2692.
- 43. (a) Guella, G.; Zanchetta, C.; Patton, B.; Miotello, A. New insights on the mechanism
 of palladium-catalyzed hydrolysis of sodium borohydride from B-11 NMR
 measurement. J. Phys. Chem. B 2006, 110, 17024–17033. (b) Patel, N.; Patton, B.;

- Zanchetta, C.; Fernandes, R.; Guella, G.; Kale, A.; Miotello, A. Pd-C powder and thin
 film catalysts for hydrogen production by hydrolysis of sodium borohydride. *Int. J. Hydrogen Energy* 2008, *33*, 287–292.
- 44. Wang, Y.; Liu, X. Catalytic Hydrolysis of Sodium Borohydride for Hydrogen
 Production Using Magnetic Recyclable CoFe₂O₄-Modified Transition-Metal
 Nanoparticles. ACS Appl. Nano Mater. 2021, 4, 11312–11320.
- 45. Wu, C.; Guo, J.; Zhang, J.; Zhao, Y.; Tian, J.; Isimjan, T. T.; Yang, X. Palladium
 nanoclusters decorated partially decomposed porous ZIF-67 polyhedron with ultrahigh
 catalytic activity and stability on hydrogen generation. *Renew Energy* 2019, *136*, 1064–
 1070.
- 46. Xu, F.; Liu, X. Magnetic Co-Pd/C Nanocomposites for Hydrogen Evolution upon the
 Hydrolytic Dehydrogenation of NH₃BH₃, NaBH₄, and Me₂NHBH₃. *ACS Appl. Nano Materials* 2021, *4*, 7479–7485.
- 47. Quach, Q.; Biehler, E.; Abdel-Fattah, T. M. Synthesis of Palladium Nanoparticles
 Supported over Fused Graphene-like Material for Hydrogen Evolution Reaction.
 Catalysts 2023, *13*, 1117.
- 48. Huda, N. U.; Ul-Hamid, A.; Khan, M. A. Shabnam Shahida, S.; Muhammad Zaheer, M.
 Mesoporous Silica (MCM-41) Containing Dispersed Palladium Nanoparticles as
 Catalyst for Dehydrogenation, Methanolysis, and Reduction Reactions. *ChemPlusChem* 2023, 88, e202300338.
- 49. Al-Msrhad, T. M. H.; Devrim, Y.; Uzundurukan, A.; Budak, Y. Investigation of
 hydrogen production from sodium borohydride by carbon nano tube-graphene
 supported PdRu bimetallic catalyst for PEM fuel cell application. *Int. J. Energy Res.*2022, 46, 4156–4173.

- 1062 50. Kotkondawara, A. V.; Rayalu, S. Enhanced H₂ production from dehydrogenation of
 1063 sodium borohydride over the ternary Co_{0.97}Pt_{0.03}/CeO_x nanocomposite grown on CGO
 1064 catalytic support. *RSC Adv.* 2020, *10*, 38184–38195.
- 51. Fu, F.; Wang, C.; Wang, Q.; Martinez-Villacorta, A. M.; Escoba, A.; Chong, H.; Wang,
 X.; Moya, S.; Salmon, L.; Fouquet, E.; Ruiz, J.; Astruc, D. Highly Selective and Sharp
 Volcano-type Synergistic Ni₂Pt@ZIF-8-Catalyzed Hydrogen Evolution from Ammonia
 Borane Hydrolysis. J. Am. Chem. Soc. 2018, 140, 10034–10042.
- Saha, S.; Basak, V.; Dasgupta, A.; Ganguly, S.; Banerjee, D.; Kargupta, K. Graphene
 supported bimetallic G–Co–Pt nanohybrid catalyst for enhanced and cost-effective
 hydrogen generation. *Int. J. Hydrogen Energy* 2014, *39*, 11566–11577.
- 1072 53. Patel, N.; Fernandes, R.; Miotello, A. Hydrogen generation by hydrolysis of NaBH4
 1073 with efficient Co-P-B catalyst: A kinetic study. *J. Power Sources* 2009, *188*, 411–420.
- 1074 54. Peña-Alonso, R.; Sicurelli, A.; Callone, E.; Carturan, G.; Raj, R. A picoscale catalyst
 1075 for hydrogen generation from NaBH₄ for fuel cells. *J. Power Sources* 2007, *165*, 315–
 1076 323.
- 1077 55. (a) Shang, Y.; Chen, R. Semiempirical Hydrogen Generation Model Using
 1078 Concentrated Sodium Borohydride Solution. *Energy Fuels* 2006, *20*, 2149–2154. (b)
 1079 Guella, G.; Zanchetta, C.; Patton, B.; Miotello, A. New Insights on the Mechanism of
 1080 Palladium-Catalyzed Hydrolysis of Sodium Borohydride from ¹¹B NMR
- 1081 Measurements. J. Phys. Chem. B 2006 110, 17024–17033.
- 56. G. Guella, G.; B. Patton, B.; A. Miotello, A. Kinetic Features of the Platinum Catalyzed
 Hydrolysis of Sodium Borohydride from ¹¹B NMR Measurements. *J. Phys. Chem. C*2007, *111*, 18744–18750.
- 1085 57. Wang, C.; Tuninetti, J.; Wang, Z.; Zhang, C.; Ciganda, R.; Salmon, L.; Moya, S.; Ruiz,
- 1086 J.; Astruc, D. Hydrolysis of Ammonia-Borane over Ni/ZIF-8 Nanocatalyst: High

- 1087 Efficiency, Mechanism, and Controlled Hydrogen Release. J. Am. Chem. Soc. 2017,
 1088 139, 11610–11615.
- 58. Li, Z.; He, T.; Liu, L.; Chen, W.; Zhang, M.; Wu, G.; Chen, P. Covalent triazine
 framework supported non-noble metal nanoparticles with superior activity for catalytic
 hydrolysis of ammonia borane: from mechanistic study to catalyst design. *Chem. Sci.*2017, 8, 781–788.
- 1093 59. Na, K.; Choi, K. M.; Yaghi, O. M.; Somorjai, G. A. Metal Nanocrystals Embedded in
 1094 Single Nanocrystals of MOFs Give Unusual Selectivity as Heterogeneous Catalysts.
 1095 Nano Lett 2014, 14, 5979–5983.
- 1096 60. Retnamma, R.; Novais, A. Q.; Rangel C. M. Kinetics of hydrolysis of sodium
 1097 borohydride for hydrogen production in fuel cell applications: A review. *Int. J.*1098 *Hydrogen Energy* 2011, *36*, 9772–9790.
- 1099 61. (a) Kalidindi, S. B.; Sanyala, U.; Jagirdar, B. R. Nanostructured Cu and Cu@Cu₂O core
 1100 shell catalysts for hydrogen generation from ammonia–borane. *Phys. Chem. Chem.*1101 *Phys.* 2008, *10*, 5870–5874. (b) Ma, H.; Na, C. Isokinetic Temperature and Size1102 Controlled Activation of Ruthenium-Catalyzed Ammonia Borane Hydrolysis. *ACS*1103 *Catal.* 2015, *5*, 1726–1735.
- 62. (a) Mori, K.; Masuda, S.; Tanaka, H.; Yoshizawa, K. Che, M.; Yamashita, H. 1104 1105 Phenylamine-functionalized mesoporous silica supported PdAg nanoparticles: a dual 1106 heterogeneous catalyst for formic acid/CO₂-mediated chemical hydrogen delivery/storage. Chem. Commnun. 2017, 53, 4677-4680. (b) Masuda, S.; Mori, K.; 1107 Futamura, Y.; Yamashita, H. PdAg Nanoparticles Supported on Functionalized 1108 1109 Mesoporous Carbon: Promotional Effect of Surface Amine Groups in Reversible Hydrogen Delivery/Storage Mediated by Formic Acid/CO₂. ACS Catal. 2018, 8, 2277-1110 1111 2285.

1112	63. Shen, J.; Chen, W.; Lv, G.; Yang, Z.; Yan, J.; Liu, X.; Dai, Z. Hydrolysis of NH ₃ BH ₃
1113	and NaBH4 by graphene quantum dots-transition metal nanoparticles for highly
1114	effective hydrogen evolution. Int. J. Hydrogen Energy 2021, 46, 796-805.

- 1115 64. Yoon, C. W.; Carroll, P. J.; Sneddon, L. G. Ammonia Triborane: A New Synthesis,
- 1116 Structural Determinations, and Hydrolytic Hydrogen-Release Properties. J. Am. Chem.
- 1117 Soc. **2009**, *131*, 855–864.