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YAL SOCIETY CHEMISTRY

# Journal Name

# ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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# Trimetallic NiFePd nanoalloy catalysed hydrogen generation from alkaline hydrous hydrazine and sodium borohydride at room temperature

Debaleena Bhattacharjee and Subrata Dasgupta \*

A simple, surfactant-assisted, room temperature synthetic route based on coreduction of Ni, Fe and Pd salts by sodium borohydride has been developed for the synthesis of trimetallic Ni-Fe-Pd nanocatalysts. The catalysts were characterised by XRD, FESEM, EDX, TEM, HRTEM, SAED and XPS studies and their catalytic activity and selectivity towards hydrogen generation from hydrous hydrazine and sodium borohydride were studied at room temperature. The support free nanoparticles possess good dispersion and small particle size revealing excellent catalytic performance for the complete decomposition of hydrous hydrazine and hydrolysis of sodium borohydride at room temperature. The recycle test results of the nanocatalyst show no significant decrease in catalytic activity over five cycles. It is believed that the trimetallic NiFePd catalyst will provide a process of preparing hydrogen gas in situ, in other words, instantly upon demand of a selected, hydrogen consuming device or process. The results presented here with a high performance catalyst system having low noble metal content offer a new prospect for on-board hydrogen production system.

## 1. Introduction

Catalysts are of fundamental importance for the worldwide production of different chemicals (both bulk and fine chemicals) and fuels that are sustainable, high in energy density and efficiency <sup>1-2</sup>. They are often being utilized by the chemical industries to do reactions near to ambient temperature as is practical, thus keeping energy usage and costs down. As hydrogen is an attractive alternative fuel to meet ever growing energy requirements while reducing the reliance on fossil fuels along with their associated environmental and resource problems so, generation of hydrogen from small hydrogen storage molecules (e.g., hydrazine, sodium borohydride, formic acid etc.) using new and better catalysts capable of showing maximum efficiency as well as selectivity at ambient reaction conditions is imperative <sup>3-6</sup>. Bi/trimetallic nanoparticles (BMNPs/TMNPs) formed by incorporation of transition metal with noble metal are found to be effective in the field of catalysis due to their unique role of controlling the activity, selectivity and stability as catalysts <sup>3-13</sup>. The hetero-metallic bond formation with the introduction of other metals results from the inter-metallic charge transfer or orbital hybridization of the metals. As a consequence of the bi/trimetallic union, the electronic-structural modifications drastically influence the catalytic performance of the mixed-metal catalyst systems showing enhancement in specific properties at an optimum composition because of the synergistic effect of the

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composition <sup>14-17</sup>. Storing and transporting of hydrogen safely and efficiently is one of the major technological barriers in the widespread application of hydrogen-fuelled cells (e.g., proton exchange membrane fuel cells (PEMFCs))<sup>18-24</sup>.Recent developments in this direction have suggested hydrous hydrazine (H<sub>2</sub>NNH<sub>2</sub>.H<sub>2</sub>O), a liquid over a wide range of temperature (213-392 K) with a hydrogen content as high as 8%, easy recharging as a liquid, as a promising material for hydrogen storage <sup>25-29</sup>, since it will only produce nitrogen in addition to hydrogen via a complete decomposition reaction  $H_2NNH_2 \rightarrow N_2 + 2H_2$  (pathway 1). However, to maximise the usability of hydrazine as a hydrogen storage material, one should avoid the undesired reaction  $3H_2NNH_2 \rightarrow 4NH_3 + N_2$ (pathway 2). The reaction pathways are dependent on the catalyst used and the reaction conditions. Therefore, the development of highly selective, efficient and economic catalysts for fast hydrogen release as and when required at low temperature is urgently important for practical applications. Aiming at achieving this goal, much effort has been devoted to the synthesis of metal catalysts for accelerating the hydrogen generation from N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O among which noble metals (e.g., Rh, Pt) or their bimetallic alloy catalysts<sup>26-33</sup> are found to be rather efficient under moderate conditions. Alternatively, efforts developing further were directed in supported/unsupported cost effective non-noble metal bi/trimetallic nanocatalysts (e.g., Ni, Fe, Mo, Cu, Fe etc.) for the decomposition of hydrous hydrazine <sup>13,16,34-39</sup>. Our recent keen studies on bi/trimetallic nanoparticle catalysed hydrous hydrazine decomposition to hydrogen and nitrogen reveal that NiFe has emerged as a central component for many of the active metallic catalysts as these components are inexpensive and proficient as hydrogen generation catalysts. However, in the literature, it is reported that although great progress has

DOI: 10.1039/x0xx00000x

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been achieved with NiFe bimetallic nanoparticles, they are catalytically inefficient for the decomposition of hydrous hydrazine at room temperature (298 K) but are active at elevated temperature i.e, above 70 °C 40. Also, for the supported NiFe nanocatalysts there is one such report on room temperature hydrogen generation<sup>16</sup> where the work describes a bifunctional NiFe-alloy/MgO catalyst obtained via calcination-reduction process of NiFeMg-layered double hydroxides (LDHs), which exhibits 100% conversion of N<sub>2</sub>H<sub>4</sub>·H<sub>2</sub>O and up to 99% selectivity towards H<sub>2</sub> generation at room temperature. Their catalyst synthesis procedure involves higher temperature, multistep treatment and thus energy intensive. In that respect efforts are made but by now there is only one report on a trimetallic system where there is inclusion of Mo along with NiFe in order to generate hydrogen at 50 °C<sup>14</sup> from hydrous hydrazine. So it is evident that there is dearth of studies regarding the modification of NiFe system in detail, like studying the performance of catalytic dehydrogenation of hydrous hydrazine by incorporating noble metal into the NiFe moiety. This inspired us to fabricate a trimetallic catalyst system  $Ni_xFe_xPd_{100-2x}$  (x = 25, 30, 35, 40, 45) which is composed of non-noble metals (Ni and Fe) along with a nobel metal palladium, as a constituent of the active catalyst system for the purpose of achieving excellent catalytic activity and overcoming the drawbacks of high temperature hydrogen generation by NiFe catalyst simultaneously. The present work demonstrates that in contrast to the catalytic inactivity of NiFe nanoparticles, a significant enhancement in the catalytic performance of  $Ni_xFe_xPd_{100-2x}$  (x = 25, 30, 35, 40, 45,) nanoparticles has been observed at 298K for hydrous hydrazine decomposition and also with a slender increase in the reaction temperature i.e., 318°C.

In this work, we focused on the synthesis of trimetallic  $Ni_xFe_xPd_{100-2x}$  (x = 25, 30, 35, 40, 45) nano catalysts in a verv simple soft chemical method and its application for the  $H_2$ generation from hydrazine decomposition. The activity of the synthesized  $Ni_xFe_xPd_{100\mbox{-}2x}$  nanocatalyst was also documented towards the hydrolysis of alkaline sodium borohydride (NaBH<sub>4</sub>) at 298K which stands out as promising storage materials for delivering H<sub>2</sub> gas to fuel cells due to its high hydrogen storage capacity (10.8 wt%) and potentially safe operation. Here, we addressed a catalyst system that is capable of catalysing two very important dehydrogenation reactions at room temperature exhausting hydrous hydrazine and sodium borohydride by varying the composition of the active metal, palladium, in the active site. This versatility is highly desirable for heterogeneous catalysts and this can start up a new trend for catalysts with multiple functionalities.

# 2. Experimental

#### 2.1 Materials

Analytical grade anhydrous PdCl<sub>2</sub>, nickel chloride, ferric chloride, NaOH, hydrazine hydrate, sodium borohydride and polyvinyl pyrrolidone (PVP) (E. Merck, India) were used without further purification. Mili-Q water was used for the preparation of all solutions.

# 2.2 Synthesis of Ni<sub>x</sub>Pd<sub>100-x</sub> BMNPs

 $Ni_xFe_xPd_{100-2x}$  (x = 25, 30, 35, 40, 45) TMNPs were synthesized by co-reduction of hydroxides of  $Pd^{2+}$ ,  $Ni^{2+}$  and  $Fe^{3+}$  in presence of PVP at 298K. 0.0053 - 0.2659 g of PdCl<sub>2</sub> (depending upon the atomic ratio of Pd in  $Ni_xFe_xPd_{100-2x}$ ) was dissolved in 20 mL of 0.1M HCl solution and stirred for 30 minutes. To that 0.1782- 0.3209 g of NiCl<sub>2</sub> was added followed by 0.1216-0.2189 g of FeCl<sub>3</sub> and stirred for another 30 minutes. The resultant mixture was then added drop wise with constant stirring to 10 mL of 1M NaOH solution containing 0.0896 g of PVP. Finally, 1mL of 2M sodium borohydride solution was added to it; immediately the black colored NPs were formed. The NPs were separated by centrifugation, severally washed with deionised water and ethanol and dried at room temperature. Pd, Ni and Fe NPs were synthesized by similar procedure for comparison.

## 2.3 Physical Characterization

The crystalline pattern of the synthesized nanopowders were characterized using X-ray diffractometer (XRD, Philips 1710, USA) with CuK $\alpha$  radiation ( $\alpha = 1.541$  Å). The spatial. morphological. compositional micro-structural and investigations were carried out with field-emission scanning electron microscopy (FESEM: model Leo, S430i, U. K.), transmission electron microscopy (TEM, G2 30ST, FEI Company, USA operating at 300 kV), high-resolution TEM (HRTEM), energy-dispersive X-ray spectroscopy (EDX), TEM energy dispersion spectroscopy (TEM-EDS), selected area electron diffraction (SAED) and X-ray photoelectron spectroscopy (PHI 5000 Versa Probe II, ULVAC-PHI, INC., USA using a monochromatic Al Ka X-ray source (1486.6 eV)). Specific surface area value is calculated from the Adsorptiondesorption nitrogen isotherms obtained using Quantachrome instruments NOVA4000e. A gas chromatograph (YL Instrument 6500GC system, Column: HP-PLOT/Q, HP-Molesieve) connected to a thermal conductivity detector (Valco Instruments Co. Inc.) was used for gas analysis.

#### 2.4 Decomposition of Hydrous Hydrazine

The catalytic decompositions of Hydrazine were carried out under Ar atmosphere in a three-necked impinger. 1.25 ml of 4M Hydrazine was added from the burette to weighed amount of catalyst dispersed in alkaline aqueous suspension in the impinger (deaired by Ar purging) and the volume was made up to 10ml. The gas evolution was monitored by displacement of water from a burette attached to another neck of the impinger. The generated gas was collected in Tedlar bags for gas chromatographic measurements. The molar ratios of catalyst: Hydrazine (n <sub>catalyst</sub> / n <sub>hydrazine</sub>) were kept constant (1:10) for all cases.

### 2.5 Recycle test of Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> catalysts

The Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> catalysts used for hydrazine decomposition reactions were separated by ultracentrifugation, washed several times with distilled water and then re-dispersed in water. The re-dispersed Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> suspension was directly used for the hydrazine decomposition reactions as before to ensure the recyclability of the Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> catalysts.

## 3. Results and Discussion

XRD profiles (Fig.1) of Pd, Ni, Fe and  $Ni_xFe_xPd_{100-2x}$  (x = 30, 35, 40, 45) NPs synthesized under same experimental conditions reveal face centered cubic (fcc) pattern of the prepared nanocatalysts. The XRD pattern of the as prepared Pd, Fe and Ni NPs exactly matches with the literature reported values (JCPDS, 1995, File no. 05-0681 for Pd, 52-0513 for Fe and 65-0380 for Ni) indicating the formation of phase pure NPs

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Fig. 1 XRD patterns of (a) Fe, (b) Ni, (c)  $Ni_{45}Fe_{45}Pd_{10}$ , (d)  $Ni_{40}Fe_{40}Pd_{20}$ , (e)  $Ni_{35}Fe_{35}Pd_{30}$ , (f)  $Ni_{30}Fe_{30}Pd_{40}$  and (g) Pd NPs.

only. The trimetallic Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> NPs show only one visible diffraction peak corresponding to the (111) plane of palladium. The absence of characteristic peak of pure Pd, Fe and Ni in the XRD of Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> NPs indicate that the prepared Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> NPs are composed of trimetallic phase rather than a physical mixture of monometallic Pd, Fe and Ni NPs. The shift in the 20 values toward lower angles as compared to pure Ni and Fe with increasing the Pd content suggest that the interplanar spacing of the Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> NPs changes with the composition of the feed molar ratio of Pd to Ni and Fe. This specific trend is indicative of alloy formation where the lattice expansion occurred (from 3.577 Å for Ni<sub>45</sub>Fe<sub>45</sub>Pd<sub>10</sub> to 3.684 Å for Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub>) with an increase in Pd content due to the substitution of larger palladium atoms for smaller nickel and iron atoms.

The TEM bright field (Fig. 2a), dark field images (Fig 2b) and SAED (inset) of the  $Ni_{30}Fe_{30}Pd_{40}$  revealed the presence of highly dispersed irregularly shaped NPs with good crystallinity as evidenced from the clearly resolved fringes in the inset (Fig 2a). The nanoparticles are of extremely small size, viz. 2-3 nm, some of them are even less than 2 nm (Fig 2a). The rings in SAED pattern are very broad (Fig 2b), i.e., 311 and 200 rings merge to appear as one broad ring. The reason behind such broadening might be due to the extremely fine size and narrow size distribution of the synthesized nanocatalysts. The FFT images (Fig 2c and 2f) display an inter-planar spacing of 0.212 nm and 0.206 nm for  $Ni_{30}Fe_{30}Pd_{40}$  and  $Ni_{40}Fe_{40}Pd_{20}NPs$ respectively which is consistent with the data obtained from XRD measurements (0.213 nm and 0.208 nm) suggesting the formation of an alloy structure. The compositional line profiles of Ni, Fe and Pd (Fig 2d) of the Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> NPs indicate the uniform alloy composition of the NPs without significant segregation of each component. Energy-dispersive X-ray spectroscopy (EDS) point analyses of randomly chosen NPs exhibit the presence of Ni, Fe, Pd in Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> NPs (ESI, and their homogeneous distribution were also Fig.S1) supported by map scan STEM-EDX studies (ESI, Fig.S2).



Fig. 2 (a) TEM bright field, histogram and resolved fringes (inset) of  $Ni_{30}Fe_{30}Pd_{40}$ ; (b) TEM dark field and SAED pattern (inset) images of  $Ni_{30}Fe_{30}Pd_{40}$ ; (c) HRTEM and FFT images (inset) of  $Ni_{30}Fe_{30}Pd_{40}$ ; (d) compositional line profile of  $Ni_{30}Fe_{30}Pd_{40}$ ; (e) TEM bright field and histogram of  $Ni_{40}Fe_{40}Pd_{20}$  and (f) resolved fringes, SAED (inset left) and dark field (inset right) images of  $Ni_{30}Fe_{30}Pd_{40}$  NPs.

The nitrogen adsorption–desorption isotherms for the  $Ni_{30}Fe_{30}Pd_{40}$  nanocatalyst following the BET method show that the room temperature reduction treatment endows the NPs with a very high surface area of 156 m<sup>2</sup>g<sup>-1</sup> (ESI, Fig.S3). The X-ray photoelectron spectroscopy (XPS) results (Fig.3) of  $Ni_{30}Fe_{30}Pd_{40}$  NPs show that Pd 3d display doublet which consists of a low energy band [Pd 3d<sub>5/2</sub> at 335.4 eV] and a high energy band [Pd 3d<sub>3/2</sub> at 340.7 eV] of core level of Pd (0). Meanwhile, signals with binding energies of Ni [2p<sub>3/2</sub>] at 852.5 eV and 855.87 eV can be attributed to the core level of Ni (0) and Ni (II) respectively. XPS analysis suggests that the surface of nickel is partly oxidized. The surface of iron is fully oxidized, as the peak at 710.55 eV corresponding to Fe<sub>2</sub>O<sub>3</sub> was found (Fig 3).

The formation of thin oxidised layer on the surface of mixed metal catalyst system containing Ni and Fe, which are very sensitive to air, as is evidenced from XPS spectrum, is a very common phenomenon<sup>40</sup>. This arises due to the exposure of the sample in air and can be removed by Ar sputtering<sup>40</sup>. (ESI, FigS4). The spectrum obtained after sputtering reveals the Ni

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 $[2p_{3/2}]$  and  $[2p_{1/2}]$  features with binding energies of 852.5eV and 869.7 eV, respectively which can be attributed to Ni(0) and the Fe  $[2p_{3/2}]$  and  $[2p_{1/2}]$  features with binding energies of 707.2eV and 720.2 eV, respectively for Fe(0). The binding energies for Pd 3d shifted to higher value <sup>41</sup> and for Ni 2p and Fe 2p shifted to lower value <sup>30</sup> in Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> NPs as compared to the core level pure Pd , Ni and Fe NPs respectively. These binding energy shifts of core electrons demonstrate that some electrons are transferred from Pd to Ni and Fe causing changes in the bulk charge around the atomic site in Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> NPs. Thus, the XPS study firmly supports the alloy structure of Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> NPs.



Fig.3 XPS spectra of Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub>NPs

3.1 Catalytic decomposition of hydrous hydrazine



4 (a) Time profile decomposition of 10 mL of 0.5 M hydrous hydrazine (hydrazine: catalyst =10:1) using (a)  $Ni_{45}Fe_{45}Pd_{10}$ , b) $Ni_{25}Fe_{25}Pd_{50}$ , (c)  $Ni_{40}Fe_{40}Pd_{20}$ , (d) $Ni_{35}Fe_{35}Pd_{30}$ , (e)  $Ni_{30}Fe_{30}Pd_{40}$  at 298K.



4 (b) Time profile decomposition of 10 mL of 0.5 M hydrous hydrazine (hydrazine: catalyst =10:1) using (a)  $Ni_{45}Fe_{45}Pd_{10}$ , (b) $Ni_{25}Fe_{25}Pd_{50}$ , (c)  $Ni_{40}Fe_{40}Pd_{20}$ , (d) $Ni_{35}Fe_{35}Pd_{30}$ , (e) $Ni_{30}Fe_{30}Pd_{40}$  at 318K.

Catalytic performances of the  $Ni_xFe_xPd_{100-2x}$  (x = 25, 30, 35, 40, 45) NPs for the decomposition of hydrous hydrazine to hydrogen were initiated with the introduction of hydrazine monohydrate into the reactor containing an alkaline suspension of catalysts kept at 298K. To investigate the dependence of hydrogen generation on the Ni/Fe/Pd ratios, the Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub> nanocatalysts with a range of Pd content (x = 25-45) have been studied (Fig.4). The concentration of NaOH (0.4M) is optimized by taking different amounts of NaOH for the same catalytic reaction (ESI, FigS5). The resulting gas was identified by a gas chromatograph connected to a thermal conductivity detector and the quantity was measured volumetrically by displacement of water from a burette for the evaluation of hydrogen selectivity. It can be seen that Pd is the key active element of all the prepared catalysts. Monometallic Pd, Fe, Ni and bimetallic NiFe NPs are inactive towards hydrogen generation from alkaline hydrous hydrazine at 298K. But when Pd is present along with Ni and Fe in NPs the activities of Ni<sub>x</sub>Fe<sub>x</sub>Pd<sub>100-2x</sub>(x=25-45) increased appreciably and it is observed that three of the catalysts namely Ni30Fe30Pd40, Ni<sub>35</sub>Fe<sub>35</sub>Pd<sub>30</sub> and Ni<sub>40</sub>Fe<sub>40</sub>Pd<sub>20</sub> has generated 3 equivalents of gas at 298K in 75, 153 and 292 minutes respectively (Fig 4a). The physical mixture of Ni, Fe and Pd NPs was also found to be inactive toward hydrogen generation from hydrous hydrazine under similar reaction conditions at 298K. These further confirm that the presence of three metals on the catalytic active sites is critical only in the form of nanoalloy (electronically modified) and not as the separate metals. Also, the high catalytic performance of Ni30Fe30Pd40 nanocatalysts for hydrazine decomposition in aqueous solution compared to the analogously synthesized Ni<sub>25</sub>Fe<sub>25</sub>Pd<sub>50</sub>, Ni<sub>35</sub>Fe<sub>35</sub>Pd<sub>30</sub>, Ni40Fe40Pd20 and Ni45Fe45Pd10 nanocatalysts indicate that alloying of Ni and Fe with Pd in a specific combination has positive effect on the hydrogen selectivity in contrast to the other compositions despite of the presence of Pd to a larger extent. It is worth noting that raising the reaction temperature to 318 K, only slightly higher than room temperature, makes it possible to achieve 100% H2 selectivity by the same Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> nanocatalyst in 37 minutes only (Fig 4b). However, no further change in H<sub>2</sub> selectivity was observed at higher temperatures, only the reaction completion time was reduced (i.e., 35minutes at 318K to 27minutes at 323K) for

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Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> nanocatalyst, (ESI, FigS6). The recycle test reveals that the  $\mathrm{Ni}_{30}\mathrm{Fe}_{30}\mathrm{Pd}_{40}$  nanocatalyst shows no significant decrease in catalytic activity over 5 cycles (ESI, FigS8). The gaseous products were identified as the mixture of H<sub>2</sub> and N<sub>2</sub> only as analysed by gas chromatography (ESI, Fig.S9). The absence of trace ammonia as a product of the reaction was confirmed by Nessler's test <sup>42</sup> (detection limit  $0.025\gamma$  NH<sub>3</sub>;  $1\gamma =$ 0.001mg) thus excluding the possibility of undesired reaction pathway 2. The TOF of Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> is calculated and found to be  $21.5 \text{ h}^{-1}$  at 323 K. This TOF value is much higher than most of the widely reported nobel metal as well as noble-metal-free heterogeneous catalysts for  $N_2H_4.H_2O$  decomposition, 9,14,28,29,30,33,40,43,44 (ESI, Table S1). This superior activity of Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> may be attributed to the electrical modification of Ni, Fe and Pd in the alloy structure of  $Ni_{30}Fe_{30}Pd_{40}$  and also the small particle size, good dispersion and very high surface area of Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> resulting from the present easy synthetic method. NaOH actually acts as a promoter for the catalytic reaction 9,33. Besides promoting the reaction kinetics, the alkaline solution also helps to inhibit the formation of NH3

In order to obtain the activation energy (Ea) for the decomposition of  $N_2H_4$ . $H_2O$  catalysed by the  $Ni_{30}Fe_{30}Pd_{40}$  NPs, the reaction was carried out at different temperatures (298K-323K) and the results are shown in ESI, Fig. S6. The Arrhenius plot of ln TOF vs. 1/T for this catalyst is plotted in ESI, Fig.S7 from which Ea is calculated as 40.0 kJ mol<sup>-1</sup>, which is very similar to the previously reported values for the catalytic decomposition of  $N_2H_4.H_2O.^{13,44-45}$ .



Fig 5 Mechanistic decomposition of hydrazine by pathway:

$$H_2NNH_2 \rightarrow N_2 + 2H_2$$

If mechanistic aspect of hydrazine decomposition is considered<sup>46</sup>, then on a catalyst surface, the stabilization of the intermediate  $N_2H_3^*$  determines the fate of the reaction by generating HN=NH species that further dissociates and ultimately leads to the formation of hydrogen and nitrogen by pathway:  $H_2NNH_2 \rightarrow N_2 + 2H_2$  (Fig 5). On the other hand if the intermediate  $N_2H_3^*$  dissociates to generate NH<sub>2</sub>\* radical, by breaking the N–N single bond which gives enough stability to hydrazine then further cleavage of the high energy N–H bond becomes difficult, thereby favouring the combination of \*NH<sub>2</sub> and \*H radicals to form ammonia<sup>47-50</sup>. As in the present catalyst system there is no ammonia formation so the reaction must have followed the desired pathway through the stabilization of the

intermediate N<sub>2</sub>H<sub>3</sub>\*. The complete decomposition reaction is initiated by the coordination of hydrazine to metal surface followed by an oxidative insertion of metal via N-H bond activation<sup>51-53</sup>. An abundance of NH adsorbed on the metal surface or the stabilization of metal-bound HN=NH as a transient intermediate is crucial and leads to the release of N2 and H2 by selective activation of the N-H bond over the N-N bond on the metal surface<sup>54-56</sup>. The observations made in the present work make it reasonable to propose that the alloying of Ni, Fe and Pd leads to a modification of the catalyst surface through incorporation of considerable intermetallic electronic interactions and accordingly the catalyst surface significantly tunes its interactions with hydrazine thereby enhancing the stability of the transient intermediates on the catalyst surface preferentially by pathway 1 over pathway 2 for its complete decomposition to hydrogen and nitrogen at 298K. The above results strongly support the conclusion that the catalyst performance is substantially governed by its structure and composition resulting from the introduction of new components. Considering the poor catalytic performance of the mono/bimetallic counterparts where Pd, Fe, Ni and NiFe are inactive for the catalytic decomposition of alkaline hydrous hydrazine at room temperature, the interaction between Ni, Fe and Pd in the NiFePd alloy outcomes in significant improvement in hydrogen generation at ambient reaction conditions.

## 3.2 Catalytic hydrolysis of sodium borohydride:

NaBH<sub>4</sub>, a very common promising hydrogen storage material due to its high hydrogen storage capacity (10.8 wt%) and potentially safe operation, is widely used to examine the efficiency of newly synthesized catalysts. To evaluate the efficacy of our synthesized NPs of different compositions, the catalysts are used towards the hydrolysis of alkaline NaBH<sub>4</sub> in order to generate hydrogen at room temperature.

When catalysts are added in alkaline  $NaBH_4$  solution, the release of hydrogen takes place via the following reaction <sup>57</sup>:

NaBH<sub>4</sub> + 2H<sub>2</sub>O 
$$\longrightarrow$$
 NaBO<sub>2</sub> + 4H<sub>2</sub>  $\uparrow$   
 $\Delta H = -217 \text{ kJ mol}^{-1}$  (1)

The reaction is exothermic and the by-product sodium metaborate (NaBO<sub>2</sub>) is nontoxic and can be recycled as the starting material for synthesizing NaBH<sub>4</sub><sup>58</sup>. Since NaBH<sub>4</sub> undergoes self-hydrolysis at ambient temperature when stored in water solution, NaOH-stabilized NaBH<sub>4</sub> solutions is used for catalytic hydrogen generation from NaBH<sub>4</sub>.

Catalytic performances of the  $Ni_xFe_xPd_{100-2x}$  (x = 35, 40, 45) NPs for the hydrolysis of sodium borohydride to hydrogen were carried out by adding alkaline NaBH<sub>4</sub> (0.1891 g of NaBH<sub>4</sub> in 10mL of 5M NaOH) into the reactor containing the measured quantity of the catalysts (catalyst: borohydride 1:10) of varying composition kept at 298K.

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DOI: 10.1039/C5TA05814G Journal Name



Fig. 6 Time profile decomposition of 10 mL of 0.5 M sodium borohydride (sodium borohydride: catalyst =10:1) using  $Ni_xFe_xPd_{100-2x}$  (x = 35, 40, 45) NPs at 298K.

Fig 6 presents the comparative study of the volume of hydrogen generation as function of time using  $Ni_xFe_xPd_{100-2x}$  (x = 35, 40, 45) catalyst powder at 298K. At first, there is a delay time (induction time) in which reaction rate is low. The delay or induction time can be assigned to a surface restructuring time necessary to transfigure the metal nanoparticles as an active catalyst. Hence, a rearrangement of the surface atoms seems to be necessary to create catalytically active sites 59-60. The mechanism of hydrolysis of sodium borohydride is clearly explained in literature<sup>61</sup>. The mechanism proposed most recently by Pena-Alonso et al.<sup>62</sup> involves the reversible chemisorption of BH4 on the catalyst surface, which produces M-BH3 and M-H intermediate species The M-H species reacts with H<sub>2</sub>O to produce H<sub>2</sub> and BH<sub>3</sub> (OH). According to the latest <sup>11</sup>B NMR measurements by Guella et al. <sup>63-64</sup>, the ratecontrolling step of the hydrolysis reaction of NaBH<sub>4</sub> is the cleavage of the water O-H bond. During the course of catalytic decomposition of NaBH<sub>4</sub> using  $Ni_xFe_xPd_{100-2x}$  (x = 35, 40, 45), the total hydrogen yield was >99% of the theoretically expected value based on Eq. (1). Among the  $Ni_xFe_xPd_{100-2x}$  (x = 35, 40, 45) NPs, it is observed that the hydrogen generation rate is fastest in the case of Ni<sub>40</sub>Fe<sub>40</sub>Pd<sub>20</sub> nanocatalyst (within 4 minutes the reaction is complete) at 298K. On the other hand, it is found that the other compositions Ni<sub>35</sub>Fe<sub>35</sub>Pd<sub>30</sub> (8 minutes) and Ni<sub>45</sub>Fe<sub>45</sub>Pd<sub>10</sub> (11 minutes) takes much more time to complete the reaction at 298K. For the trimetallic nanocatalyst the hydrogen generation rate per unit mass could be up to 3343.28, 1555.55, and 1313.78 ml min<sup>-1</sup> g<sup>-1</sup> catalyst for Ni<sub>40</sub>Fe<sub>40</sub>Pd<sub>20</sub>, Ni<sub>35</sub>Fe<sub>35</sub>Pd<sub>30</sub> and Ni<sub>45</sub>Fe<sub>45</sub>Pd<sub>10</sub> respectively at 298K, which are all superior to crystal state Ni (19.5 ml min-1 g-1 catalyst) and Raney Ni (228.5 ml min-1 g-1)<sup>65</sup>. The comparative data for rate of gas generation for various catalysts are given<sup>66-76</sup> in ESI, Table S2.

The high catalytic performance of  $Ni_{40}Fe_{40}Pd_{20}$  nanocatalysts for borohydride hydrolysis in alkaline solution compared to the analogously synthesized  $Ni_{35}Fe_{35}Pd_{30}$  and  $Ni_{45}Fe_{45}Pd_{10}$ nanocatalysts indicate that alloying of Ni and Fe with Pd in a specific combination has positive effects on the gas generation rate. Thus, increase or decrease in Ni, Fe or Pd content from  $Ni_{40}Fe_{40}Pd_{20}$  results in the decrease of H<sub>2</sub> selectivity. Also electron enriched metal active sites are necessary to facilitate the catalysis reaction. These electrons are provided by the alloying Pd to the active metal sites, as observed in the XPS studies of  $Ni_{40}Fe_{40}Pd_{20}$  (ESI, Fig.S10) where the binding energies for Pd(0)3d [3d<sub>5/2</sub> at 334.7 eV,  $3d_{3/2}$  at 340.08 eV] shifted to higher value and for Ni(0) [2p<sub>3/2</sub> at 851.9 eV] shifted to lower value as compared to the core level pure Pd(0)<sup>41</sup> and Ni(0) NPs<sup>30</sup> respectively although the Fe [2p<sub>3/2</sub> at 709.9eV] surface seems to be oxidized. These thin oxidized layer formed during exposure of the sample can be removed by Ar sputtering as is observed in the previous case of Ni<sub>30</sub>Fe<sub>30</sub>Pd<sub>40</sub> NPs. These shifts in electronic spectra evidences change in the bulk charge around the atomic site in Ni<sub>40</sub>Fe<sub>40</sub>Pd<sub>20</sub> NPs and play a significant role in enhancing the catalytic activity due to synergistic electronic contribution from all the three elements in the trimetallic system.

## 4. Conclusion

In summary, we report a highly active trimetallic Ni-Fe-Pd nanocatalyst prepared by a soft chemical method which exhibits 100% hydrogen selectivity for complete decomposition of hydrous hydrazine at 298K. The synthesized nanoalloy catalyst significantly improves the kinetic properties for the catalytic dehydrogenation of hydrazine at room temperature as well as at slightly elevated temperature. The catalyst also stimulates hydrolysis of sodium borohydride within 4 minutes under alkaline and ambient reaction conditions. It is believed that this low cost, efficient and selective H<sub>2</sub> generation system at room temperature will promote new opportunities in the development of high-performance metal bi/trimetallic nanoparticle catalysts and also encourage the effective application of hydrous hydrogen storage material.

# Acknowledgements

The authors like to thank DST, Govt. of India (Project no. GAP0344), and CSIR, New Delhi (Project no. ESC0104) for financial support.

# Notes and references

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# **Graphical abstract**



Room temperature synthesized  $Ni_xFe_xPd_{100-2x}$  nanocatalyst exhibits improved catalytic activity towards hydrogen generation from hydrazine and borohydride under ambient reaction conditions