PAPER

Aqueous phase semihydrogenation of alkynes over
Ni–Fe bimetallic catalysts†

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Bimetallic Ni–Fe catalysts (Ni/Fe, 1:1, 1:3, and 3:1) are synthesized and explored for their catalytic activity in semihydrogenation of internal alkynes using H₂ gas in water–ethanol solution. Our findings revealed that over the Ni₁Fe₃ catalyst a high diastereoselectivity for Z-alkenes with a high conversion for a wide range of internal alkynes can be achieved at moderate reaction temperature (40 °C). Notably, the selectivity for the Z-alkenes is enhanced in the presence of *n*-butyl amine as an additive. Deuterium labeling experiments evidenced that H₂ gas becomes dissociated homolytically over the catalyst surface to hydrogenate alkynes to alkenes. Synthesized catalysts were successfully characterized by HR-TEM, SEM, XPS, EDS, P-XRD and H₂-TPD.

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Introduction

Selective semihydrogenation of alkynes to alkenes employing heterogeneous catalysts remains one of the most studied reactions for both in industry and in academia.^{1–4} Well-defined configured olefins (*E* or *Z*) are the key building blocks for the synthesis of various fine chemicals, such as vitamins and various natural products.^{1–4} In industries, the Lindlar catalyst, consisting of Pd–CaCO₃ partially poisoned with Pb(OAc)₂ and quinoline, is still the first choice for the selective semihydrogenation of alkynes to Z-alkenes.^{5,6} However, due to various disadvantages of the Lindlar catalyst (use of excess ligand and harmful Pb as a promoter), over the past decades, many catalysts have been developed based on monometallic Pd,^{7–10} Au,^{11–13} Ru,¹⁴ Rh,¹⁵ Ni,^{16–25} Co,²⁶ Fe,²⁷ and Cu (ref. 28 and 29) as well as bimetallic Pd–Ag,³⁰ Pd–Au,³¹ Pd–Ru,³² Au–Pt,³³ Pd–Cu,³⁴ Pd–Ga,³⁵ Rh–Co,³⁶ Rh–Ni,³⁷ Co–Pt,³⁸ Ni–Cu,³⁹ Ni–Fe,^{40,41} Cu–Fe,⁴¹ Ni–Ga (ref. 42 and 43) and trimetallic Cu–Ni–Fe (ref. 41) catalysts for the selective semihydrogenation of alkynes to alkenes. In this direction,

particularly, exploration of bimetallic nanoparticles have gained tremendous attention for the selective hydrogenation of alkynes as compared to monometallic catalysts, because they exhibit superior chemical and physical properties.^{30–45} For example, very recently Li *et al.* have reported Pd@Au–Pd alloy surface nanocubes for semihydrogenation of alkynes to alkenes (alkene/alkane; 91/9) using a hydrogen balloon in toluene at room temperature.³¹ Similarly, Lu *et al.* also reported bimetallic Pd–Pb alloy octahedral nanocrystal based catalysts for the semihydrogenation of alkynes.⁴⁵ Lyutakov *et al.* also explored bimetallic Au/Pt heterostructures for the selective hydrogenation of alkyne bonds, of 4-ethynylphenyl groups covalently grafted on the catalyst surface, to alkenyl or alkyl moieties using cyclohexene as a hydrogen source.³³ The Au supported surface plasmon polaritons (SPPs) activate the hydrogenation of alkynes, while the thickness of the Pt layer tunes the alkenyl *vs.* alkyl selectivity.³³ The RhNi@MOF-74 alloy catalyst also exhibited appreciably good activity for the semihydrogenation of alkynes to Z-alkenes.³⁷ Complete selectivity for 4-octene was also reported for the hydrogenation of 4-octyne over Pt and CoPt₃ catalysts using 1-octylamine as an additive, where the amine additive played a crucial role in tuning the selectivity towards the alkene product over alkane.³⁸ However, considering the high cost and scarcity of noble metals, it is highly desirable to explore non-noble metal based catalysts with high natural abundance and low cost for semihydrogenation reactions. In this direction, various non-precious metal catalysts based on Ni,^{16–25} Co,²⁶ Fe,²⁷ and Cu (ref. 28 and 29) have been employed for selective semihydrogenation reactions. Among them, development of Ni-based catalysts has received tremendous interest, because of their low cost and

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considerably high catalytic activity. Nickel metal is known for its high catalytic activity for hydrogenation of unsaturated C–C bonds, but the presence of a second metal can effectively tune the properties of Ni catalysts.⁴⁶ Liu *et al.* recently reported NiCu nanoalloy catalysts for semihydrogenation of alkynes to achieve 100% conversion at 160 °C in toluene with improved selectivity for alkenes (>70%).³⁹ Earlier, hydrogenation of 4-octyne was also explored using various monometallic (Fe, Ni, Co, and Cu) and bimetallic (NiFe, FeCo and FeCu) catalysts at room temperature under 5 bar H₂ pressure in THF.⁴⁰ Among these, FeCu and Cu nanoparticles were found to be inactive, while other bimetallic NiFe and FeCo exhibited similar activity (with intermediate selectivity for the alkene product) to the monometallic Ni, Co and Fe.⁴⁰ Ternary Cu_{3–x}Ni_xFe catalysts were reported to exhibit high selectivity for propene and ethene in a gas-phase hydrogenation reaction of propyne and ethyne, respectively, at 1 bar pressure (H₂/alkyne = 1.5) and 250 °C.⁴¹ Results inferred that the optimum Ni content and intimate contact of Cu and Ni in the Cu_{3–x}Ni_xFe catalysts was found to be essential to achieve high alkene selectivity. The literature also revealed that Fe, being low cost and abundant in nature, could be a promising metal partner to fine-tune the performance of nickel in the bimetallic Ni–Fe catalyst.^{46,47} The presence of Fe in the bimetallic Ni–Fe catalyst may influence the catalytic activity of Ni–Fe catalyst in several ways, which includes Fe to Ni electronic charge transfer, tuning of the adsorption behavior of reactants and the availability of hydrogen atoms on the catalyst surface, and hence may tune the product selectivity in hydrogenation reactions.⁴⁶ However, the development of bimetallic Ni–Fe catalysts and the investigation of their catalytic performance for the semihydrogenation of internal alkynes to the corresponding alkenes are yet to be explored in detail. Further, some of the recent reports show that the semihydrogenation of alkynes to alkenes over Ni catalysts can be achieved using NaBH₄ as a reducing agent.¹⁷ However, this methodology demands an excess of NaBH₄, because only some NaBH₄ was used for the reduction of alkynes and the rest of NaBH₄ generated hydrogen gas, which escaped from the reaction medium. Notably, the reported Ni catalysts could not catalyze this reaction in the presence of H₂ gas.¹⁷ Very recently, Huang *et al.* reported CuO rhombic dodecahedral crystals for selective semihydrogenation of alkynes in the presence of ammonia borane.²⁸ Therefore, these reports inferred that the development of highly active catalysts for the selective semihydrogenation of alkynes to alkenes required both facile activation of H₂ and suppressed over-hydrogenation reactions. Further, most of these reactions require high temperature, pressure and the use of excess inorganic hydrides (NaBH₄ and NH₃BH₃), which needs to be overcome.

Hence, on the basis of available reports, it is highly desirable to develop a low-cost and more environmentally benign catalytic system for semihydrogenation of alkynes. Further, using molecular H₂ gas as a hydrogen source is more

economical and environment friendly. Over the past few years, we developed several cost-effective and high-performance non-noble metal-based catalysts particularly bimetallic catalysts for various organic transformations.^{47–49} Herein, we have synthesized bimetallic Ni–Fe (Ni/Fe, 1 : 1, 1 : 3, and 3 : 1) alloy nanoparticles along with monometallic Ni and Fe nanoparticles and explored their catalytic activity for the semihydrogenation of alkynes to Z-alkenes using molecular H₂ as a hydrogen source at atmospheric pressure in water–ethanol solution at 40 °C. We probed several characterization tools to establish the alloy composition of Ni and Fe in the synthesized bimetallic Ni–Fe catalysts. Moreover, we also investigated the effect of Ni-to-Fe content and amine additives in tuning the selectivity towards Z-alkene products. Further, the selective semihydrogenation of a wide range of alkynes was also explored over the best performing catalysts under the optimized reaction conditions.

Results and discussion

Synthesis and characterization of bimetallic Ni–Fe catalysts

Our bimetallic Ni–Fe catalysts were prepared by co-reduction of an aqueous solution of nickel(II) chloride and ferrous(II) sulfate using an aqueous solution of sodium borohydride as a reducing agent in the presence of poly(vinylpyrrolidone) (PVP).⁴⁷ Different compositions of the bimetallic Ni–Fe catalysts were prepared by varying the Ni/Fe molar ratios (Ni/Fe, 3 : 1, 1 : 1 and 1 : 3). Analogously, monometallic Ni and Fe catalysts were also synthesized. The molar composition of Ni/Fe in the bimetallic Ni₃Fe₁, Ni₁Fe₁ and Ni₁Fe₃ catalysts were further authenticated by inductively coupled plasma optical emission spectrometry (ICP-OES) analyses, which matches well with the expected Ni/Fe composition (Table S1†). Scanning electron microscopy (SEM) images along with SEM-energy dispersive X-ray spectroscopy (EDS) and elemental mapping evidenced the presence of both Ni and Fe in the bimetallic Ni₃Fe₁, Ni₁Fe₁ and Ni₁Fe₃ catalysts (Fig. S1–S3†). The morphology and chemical composition of all the bimetallic Ni₃Fe₁, Ni₁Fe₁ and Ni₁Fe₃ catalysts were also authenticated by transmission electron microscopy (TEM), TEM-EDS point and line scan analyses (Fig. 1 and S4 and S5†). TEM images exhibited the presence of irregularly shaped nanoparticles in the bimetallic Ni–Fe catalysts (Fig. S4†). In particular, TEM images of the Ni₁Fe₃ catalyst inferred the presence of nanoparticles with an average size of *ca.* 6.5 nm (Fig. 1 and S4†). Moreover, the TEM-EDS analysis and high-angle annular dark field EDS (HAADF-EDS) elemental mapping of Ni and Fe exhibited a very similar distribution, which further indicated the co-existence of both Ni and Fe metals in the Ni₁Fe₃ catalyst. Consistent with elemental mapping, the EDS line scan profile of the Ni₁Fe₃ catalyst also indicated the co-existence of both Ni and Fe metals in the proposed composition (Fig. S5†). It can also be seen that elemental mapping of the Ni₁Fe₃ catalyst also showed the presence of C, N and O atoms, suggesting the presence of

Fig. 1 Characterization of the bimetallic Ni-Fe catalysts. (a) TEM, (b) particle size distribution (c) HR-TEM, (d) SAED, (e–g) TEM image and the corresponding elemental mapping images of Ni and Fe, and (h) TEM-EDS spectrum of the Ni_1Fe_3 catalyst. (i and j) HAADF-STEM image and corresponding EDS line scan of the Ni_1Fe_1 and (k and l) Ni_3Fe_1 catalyst, respectively, (m) P-XRD pattern of the monometallic (Ni and Fe) and bimetallic Ni_1Fe_3 , Ni_1Fe_1 , and Ni_3Fe_1 catalysts.

PVP polymers around the nanoparticles (Fig. S6†).⁵⁰ The selected-area electron diffraction (SAED) exhibited diffused ring patterns for the Ni_1Fe_3 catalyst (Fig. 1d). Moreover, the lattice spacing of the fringes in the HR-TEM image of the Ni_1Fe_3 nanoparticles was measured to be 0.21 nm, which is within the expected value of Ni ($d = 2.06$ nm) and Fe ($d = 2.08$ nm), supporting the alloy nature of the Ni_1Fe_3 catalyst (Fig. 1c). Moreover, the alloy composition of bimetallic Ni_3Fe_1 and Ni_1Fe_1 catalysts was also confirmed by the HAADF-STEM (scanning transmission electron microscopy) and EDS line scanning analyses. The EDS line scanning profiles of Ni and Fe of the randomly chosen nanoparticles of Ni_3Fe_1 and Ni_1Fe_1 catalysts corresponding to their respective HAADF-STEM images clearly supported the uniform alloy composition of the bimetallic Ni-Fe catalysts with no substantial segregation for either of the elements (Fig. 1). Moreover, these results also eliminate the formation of a core-shell structure or

other phases for the bimetallic Ni-Fe catalysts. A thin oxide coating over the nanoparticles was, however, observed in TEM images, but this could be due to the partial oxidation of the nanoparticle surface upon exposure to air during sample preparation. Hence, the above EDS point and line scanning and elemental mapping results clearly indicated the homogeneous distribution of both metals with the proposed Ni/Fe compositions in the bimetallic, Ni_1Fe_3 , Ni_1Fe_1 and Ni_3Fe_1 catalysts (Fig. 1 and S5, S7 and S8†). The powder X-ray diffraction (P-XRD) pattern of the bimetallic Ni_3Fe_1 , Ni_1Fe_1 and Ni_1Fe_3 catalysts showed a broad diffraction peak centered at a 2θ value of 40–50° which lies between the *fcc* peak of Ni (JCPDS 65-0380) and Fe (JCPDS 52-0513), further supporting the alloy composition of the metallic Ni and Fe in the bimetallic Ni-Fe catalysts (Fig. 1m).⁴⁷ The observed broad diffraction peak in the P-XRD pattern of the bimetallic Ni-Fe catalysts could be due to the smaller nanoparticles as these

Fig. 2 XPS spectra of the bimetallic Ni_3Fe_1 , Ni_1Fe_1 and Ni_1Fe_3 catalysts along with the monometallic (Ni and Fe) catalysts.

catalysts were synthesized in the presence of a PVP stabilizer.⁵⁰

The chemical states of Ni and Fe elements in the bimetallic Ni-Fe catalysts were established by high-resolution X-ray photoelectron spectroscopy (XPS). Fig. 2 shows the Ni 2p and Fe 2p spectra of the bimetallic Ni-Fe catalyst. In the Ni 2p_{3/2} spectrum of the Ni_1Fe_3 catalyst, two major fitted bands at 852.5 eV and 853.1 eV are respectively associated with the core levels of metallic Ni^0 and Ni^{2+} states.^{47,51,52} Analogously, Ni_1Fe_1 and Ni_3Fe_1 catalysts also displayed XPS peaks for Ni 2p_{3/2} with two fitted bands corresponding to the metallic Ni^0 (major) and Ni^{2+} (minor) states (Fig. 2). Notably, the fitted peak for the metallic Ni^0 is prominent and intense as compared to the Ni^{2+} band. The observed minor Ni^{2+} peaks could be due to the easy re-oxidation of Ni^0 at the surface to Ni^{2+} upon exposure to air during the sample preparation for XPS analysis. On the other hand, Fe 2p peaks were fitted with three bands for all the bimetallic Ni_3Fe_1 , Ni_1Fe_1 and Ni_1Fe_3 and the monometallic Fe catalysts. The prominent peak at 706.7 eV corresponds to the metallic Fe^0 , while peaks at 711.4 eV and 708.7 eV are associated with Fe^{3+}

and Fe^{2+} species, respectively.^{47,51,52} Therefore, the presence of peaks corresponding to Ni^0 and Fe^0 in the XPS spectra indicated the co-existence of both Ni and Fe in the bimetallic Ni_3Fe_1 , Ni_1Fe_1 and Ni_1Fe_3 catalysts. It is evident from the XPS pattern that the metallic Fe^0 species are abundant in all the bimetallic Ni_3Fe_1 , Ni_1Fe_1 and Ni_1Fe_3 catalysts, while easy re-oxidation of Fe^0 species in air probably resulted in the formation of $\text{Fe}^{2+}/\text{Fe}^{3+}$ species over the catalyst surface,^{51,52} as also observed as a thin oxide coating in the TEM images of these bimetallic Ni-Fe catalysts.

Optimization of catalytic reaction conditions

At the outset, the catalytic efficacy of the synthesized bimetallic Ni-Fe (Ni/Fe, 1:1, 1:3, 3:1) catalysts along with the monometallic Ni and Fe catalysts was investigated for semihydrogenation of alkynes using diphenylacetylene (**1a**) as a model substrate in the presence of hydrogen gas in water-ethanol solution. The results summarized in Table 1 inferred that the monometallic Ni catalyst completely hydrogenated diphenylacetylene (**1a**) to dibenzyl (**3a**), whereas the Fe catalyst was found to be inactive under analogous reaction conditions (Table 1, entries 1–2). Analogous to the Ni catalyst, the bimetallic Ni_1Fe_1 and Ni_3Fe_1 catalysts were also active for the complete hydrogenation of diphenylacetylene (**1a**) to dibenzyl (**3a**) (Table 1, entries 3 and 4). Even at a lower conversion of **1a** (75% in 3 h), the selectivity for the overhydrogenated product (**3a**) was as high as 44% over the Ni_1Fe_1 catalyst (Table 1, entry 4). On the other hand, the Ni_1Fe_3 catalyst exhibited high selectivity (70%) for the semihydrogenated products (*cis-trans*-stilbene **2a**, *Z/E*; 93/7) with 91% conversion of **1a**, under analogous reaction conditions (Table 1, entry 5, Fig. 3a). Since it is clearly seen in the TEM and XPS data that the bimetallic Ni-Fe catalysts have Ni and Fe in alloy composition, the observed catalytic performance of the Ni_1Fe_3 catalyst clearly evidenced the crucial role of the molar composition of Ni/Fe in achieving higher selectivity for alkenes.

At this stage, we also investigated the effect of the ethanol-water ratio on the conversion and selectivity of the products for the semihydrogenation of **1a** over the best performing Ni_1Fe_3 catalyst. In ethanol, the reaction could not proceed, and we recovered only reactant **1a** after the reaction (Table 1, entry 6), whereas in pure water, 12% conversion of **1a** was observed with only lower selectivity for alkene (**2a/3a**, 23/77, *Z/E*; 34/66) (Table 1, entry 7). In contrast to the above, we achieved good conversion with moderate selectivity for **2a** in the water-ethanol (v/v, 1:1) mixture, suggesting the important role of water in this reaction (Table 1, entry 5). In the literature, we found that water helps in the diffusion of hydrogen atoms on the surface of iron oxide.⁵³ Recently, similar findings were also reported by Yang *et al.* for the hydrogenation of α,β unsaturated aldehydes.⁵⁴ Therefore, these precedent reports and our experimental results evidenced that presumably water assists the diffusion of hydrogen atoms on the catalyst surface during catalytic

Table 1 Optimization of the reaction conditions for semihydrogenation of diphenylacetylene (**1a**)^a

$\text{Ph}-\text{C}\equiv\text{C}-\text{Ph} \xrightarrow[\text{Solvent, additives, H}_2 \text{ balloon, Temp.}]{\text{Catalysts}} \underbrace{\text{Ph}-\text{CH}=\text{CH}-\text{Ph}}_{\text{2a}} + \underbrace{\text{Ph}-\text{CH}=\text{CH}-\text{Ph}}_{\text{3a}}$								
Entry	Catalyst	Temp. (°C)	Time (h)	Additives	EtOH:H ₂ O	Conv. ^b (%)	Sel. ^b (2a/3a) (%)	Sel. ^b (Z/E) (%)
1	Ni	50	5	—	1:1	>99	0/>99	0/0
2	Fe	50	5	—	1:1	0	0/0	0/0
3	Ni ₃ Fe ₁	50	5	—	1:1	99	0/>99	0/0
4	Ni ₁ Fe ₁	50	5	—	1:1	>99(75) ^c	0/>99	0/0
5	Ni ₁ Fe ₃	50	5	—	1:1	91	70/30	93/7
6	Ni ₁ Fe ₃	50	5	—	1:0	0	0/0	0/0
7	Ni ₁ Fe ₃	50	5	—	0:1	12	23/77	34/66
8	Ni ₁ Fe ₃	25	5	—	1:1	57	58/42	91/9
9	Ni ₁ Fe ₃	40	5	—	1:1	83	77/23	84/16
10	Ni ₁ Fe ₃	50	5	<i>n</i> -Propyl amine	1:1	98	84/16	96/4
11	Ni ₁ Fe ₃	40	5	<i>n</i> -Propyl amine	1:1	93	91/9	91/9
12	Ni ₁ Fe ₃	40	4	<i>n</i> -Butyl amine	1:1	99	91/9	96/4
13	Ni ₁ Fe ₃	40	5	iso-Butyl amine	1:1	82	89/11	97/3
14	Ni ₁ Fe ₃	40	3	<i>n</i> -Pentyl amine	1:1	60	94/6	87/13
15	Ni ₁ Fe ₃	50	5	PPh ₃	1:1	5	>99/—	>99/0
16	Ni ₁ Fe ₃	40	5	Triethyl amine	1:1	99	30/70	80/20
17	Ni ₁ Fe ₃	40	5	NaOH	1:1	43	78/22	86/14
18	Ni/Fe ₃ O ₄ (1:3) ^d	40	4	<i>n</i> -Butyl amine	1:1	38	93/7	88/12

^a Reaction conditions: **1a** (1.0 mmol), catalyst (10 mol%), additive (0.55 mmol) under a H₂ atmosphere. ^b Conversion of **1a** and selectivity of (Z) *cis*-**2a**, (E) *trans*-**2a** and **3a** was determined by ¹H NMR. ^c **2a**/**3a**; 56/44, 3 h. ^d Ni/Fe molar ratio.

semihydrogenation reactions. Moreover, ethanol is completely miscible in water without any phase separation and the presence of ethanol also facilitates the solubility of diphenylacetylene in the ethanol–water solvent medium during the catalytic hydrogenation of alkynes to Z-alkenes

over the NiFe catalyst at 40–50 °C. Furthermore, we have also studied the effect of temperature, where we observed that performing the reaction at room temperature the activity and selectivity of the catalyst drastically decreased (Table 1, entry 8), whereas at 40 °C, 83% conversion of **1a** was achieved with 77% selectivity (Z/E; 84/16) for **2a** (Table 1, entry 9).

Q5 Fig. 3 (a) Catalytic activity of the monometallic (Ni and Fe) and bimetallic Ni–Fe catalysts for the hydrogenation of diphenylacetylene (**1a**) (Ni₁Fe₃ in the presence of *n*-butyl amine as an additive is denoted by superscript a). (b) Time dependent catalytic activity of the Ni₁Fe₃ catalyst with *n*-butyl amine as an additive.

Screening of additives

A judicious selection of additives with appropriate adsorption properties with the catalyst surface can lead to a remarkable enhancement in the selectivity for the desired product. In this regard, amine-based additives are generally known to accelerate catalytic activity for the semihydrogenation of alkynes to alkenes.^{38,55} Therefore, we made further attempts to increase the selectivity of the desired alkene product with a high Z/E ratio by employing various amine-based additives in the semihydrogenation of **1a** catalyzed over the best performing Ni₁Fe₃ catalyst at 40 °C in water–ethanol (1:1 v/v) solution. Firstly, we used *n*-propyl amine as an additive and observed a substantial increase in the selectivity for the desired alkene product (**2a**) to 84% (Z/E 96/4) as compared to 70% (Z/E 93/7) selectivity obtained for the Ni₁Fe₃ catalyst in the absence of the additive (Table 1, entries 5, 10). Notably, we observed that the apparent conversion of diphenylacetylene (**1a**) was analogous for both cases (with or without the additive) over the Ni₁Fe₃ catalyst. Earlier reports also inferred that introducing primary amines as additives may significantly tune the selectivity towards alkene products for the hydrogenation of 4-octyne over CoPt₃ and Pt

catalysts.³⁸ Analogously, high selectivity for alkene products were also reported using amine additives based on a diethylenetriamine (DETA) tridentate ligand for the hydrogenation of alkynes over Pd nanoparticles supported on boron nitride (Pd/BN).⁵⁵ Noticeably, higher selectivity for alkene products (**2a**, 91%, (*Z/E*: 91/9) with appreciably good conversion (93%) was achieved even at 40 °C (Table 1, entry 11). Reports revealed that selectivity towards alkene products can also be enhanced by tuning the steric crowding over the catalyst surface.^{38,55} Therefore, to obtain a better understanding of the role of amine additives in the selective semihydrogenation of **1a** to the *cis-trans*-alkene products (**2a**), we further employed other aliphatic amine additives having branched and long carbon chains (*n* = 4 and 5). Results showed that with the increase in the carbon chain of the linear amine additives, conversion of **1a** was also increased while maintaining the high selectivity for *Z*-stilbene (**2a**) (Table 1, entries 11–12). The observed higher activity of the Ni₁Fe₃ catalyst in the presence of *n*-butyl amine as compared to *n*-propyl amine was presumably due to the higher basicity of the former.³⁸ Further increase in the carbon chain of *n*-pentyl amine does not significantly change the conversion and selectivity for the studied reaction (Table 1, entry 14). On the other hand, a relatively lower activity was observed in the presence of branched aliphatic amines (iso-butyl amine, conv. 82%) as additives as compared to the corresponding linear amines (*n*-butyl amine, conv. 99%), presumably due to the steric effect (Table 1, entries 12–13).^{38,55} Further, the content of the additive also significantly influenced the catalytic activity, where higher selectivity for the alkene product (**2a**) was achieved with 0.55 equiv. of the *n*-butyl amine additive (Table S2†). These observations can be associated with the tuning of surface adsorption sites by the amine additives, where larger coverage of additives over the catalyst surface competes with the alkene product and hence hindered the over hydrogenation of alkenes to alkanes.^{38,55} In contrast to the amine-based additives, other additives, such as phosphine, trimethylamine and an inorganic base (NaOH) exhibited either poor conversion of **1a** or poor selectivity for the alkene (**2a**) products (Table 1, entries 15–17). Therefore, among several additives screened, *n*-butyl amine exhibited significantly tuned and high selectivity for *Z*-alkene (**2a**) with higher conversion of the alkyne (**1a**) under the optimized reaction conditions (Table 1 and Table S2†). Furthermore, to rule out the role of polyvinylpyrrolidone (PVP) in controlling the reaction selectivity,⁵⁰ we synthesized Ni₁Fe₃ nanoparticles without using PVP and investigated their activity for semihydrogenation of **1a**, with/without the *n*-butyl amine additive, under the optimized reaction conditions. Though the results (as summarized in Table S2†) inferred the loss in the catalytic activity for the Ni₁Fe₃ catalyst (synthesized without using PVP), as compared to the Ni₁Fe₃ catalyst (synthesized using PVP), the selectivity of *Z*-stilbene was not affected significantly. These findings suggest that PVP has no significant role in tuning the selectivity of the semihydrogenated product (**2a**). However, the absence of PVP

may induce the agglomeration of nanoparticles, which presumably resulted in the observed loss in the catalytic activity for the Ni₁Fe₃ catalyst synthesized in the absence of PVP. Consistent with the above results, the TEM images of the Ni₁Fe₃ catalyst, synthesized without using PVP, also displayed the agglomeration of nanoparticles (Fig. S9†). Further, dynamic light scattering (DLS) data of the aqueous-ethanol suspension of Ni₁Fe₃ nanoparticles also showed the high rate of agglomeration of Ni₁Fe₃ nanoparticles synthesized in the absence of PVP, as indicated from the distribution curves (Fig. S10†). Moreover, the P-XRD pattern of the Ni₃Fe₁ catalyst synthesized in the absence of PVP also displayed intense diffraction peaks at a 2θ value of 40–50°, as compared to those synthesized in the presence of PVP (Fig. S11†).

The time-course profile for the hydrogenation of **1a** over the Ni₁Fe₃ catalyst in the presence of the *n*-butyl amine additive indicated that the reaction time conversion of **1a** also increased with no significant loss in the selectivity for *Z*-stilbene (**2a**) (Fig. 3b). Further, the catalytic activity of the high performance Ni₁Fe₃ catalyst was also compared with several other catalysts (Ni, Ni₁Fe₁, Ni/Fe₃O₄) under the optimized reaction conditions (**1a** (1.0 mmol), catalyst (10 mol%), *n*-butyl amine (0.55 mmol), H₂ atmosphere, 40 °C). Results clearly inferred that the yield of the desired *Z*-stilbene (**2a**) for Ni and Ni₁Fe₁ catalysts was less than that for the Ni₁Fe₃ catalyst (Fig. S12†). The observed trend is analogous to that observed for the semihydrogenation reaction performed over various NiFe catalysts in the absence of the *n*-butyl amine additive (Fig. 3a and Table 1). The observed lower selectivity to *Z*-alkene over these catalysts was presumably due to their higher Ni content which is favorable for the formation of overhydrogenated products.⁴¹ These results are consistent with the earlier findings of Pérez-Ramírez *et al.*, where with the increase in the Ni content in the Cu_{3–x}Ni_xFe catalyst undesired formation of overhydrogenation alkane product was observed.⁴¹ Further, the poor conversion (38%) of **1a** over Ni/Fe₃O₄ (Ni/Fe; 1/3 similar to Ni₁Fe₃) evidenced that the atomic level interaction between Ni and Fe is crucial to achieve enhanced catalytic activity for the semihydrogenation of alkynes (Table 1, entry 18). Moreover, performing the catalytic reaction by replacing H₂ gas with other reducing agents (NaBH₄ and N₂H₄) exhibited only a moderate conversion of **1a** as compared to H₂ gas (Table S2†). Hence, higher catalytic activity for the semihydrogenation reaction of the alkyne (**1a**) over the Ni₁Fe₃ catalyst can be attributed to the high stability of adsorbed alkynes over the catalyst surface, while the selectivity for alkene (**2a**, *Z/E*) products was governed by the low stability of the adsorbed alkenes on the catalyst surface influenced by the alkyne and the amine additive.^{56,57} Furthermore, the observed traces of the unwanted dibenzyl (**3a**) product was formed *via* the second hydrogenation of alkenes, whereas *trans*-alkene was formed by *cis-trans* isomerization.^{56,57} Notably, the Ni₁Fe₃ catalyst can be magnetically recovered using an external magnet (Fig. S13†). The recovered Ni₁Fe₃

nanoparticle catalyst was reused for another catalytic run for the semihydrogenation of **1a** and achieved high selectivity (89%) for **2a** with an appreciably high diastereoselectivity ratio (*Z/E* 94:6) (Table S2,† entry 5). These findings suggest that indeed the Ni_1Fe_3 catalyst is catalytically active for the semihydrogenation of alkynes. The recovered catalyst was characterized by TEM and EDS, which indicated the co-existence of both the Ni and Fe metals in the Ni_1Fe_3 catalyst with no significant segregation for either of the metals (Fig. S14†). However, the activity decreased in further catalytic runs, presumably due to the oxidation of the catalysts during the catalytic reaction, as also suggested by the XPS analysis of the spent catalyst (Fig. S15†).

Heterogeneity test of the Ni_1Fe_3 catalyst

We performed heterogeneity experiments as shown in Scheme 1, where under the optimized reaction conditions, semihydrogenation of diphenylacetylene (**1a**) was performed over the Ni_1Fe_3 catalyst. After 2 h of the reaction, the reaction mixture was separated into two parts – first part was analyzed by ^1H NMR, while in the second part the Ni_1Fe_3 catalyst was removed and the reaction was allowed to run without the catalyst for a longer reaction time (3 h) using a H_2 balloon.

The result inferred that the reaction could not proceed in the absence of the Ni_1Fe_3 catalyst, hence supporting the heterogeneous nature of the Ni_1Fe_3 catalyst for the semihydrogenation of alkynes. Moreover, ICP-OES was used to identify traces of metals leached during the catalytic reaction. The results are summarized in Table S1.† As expected, there was no change in the molar composition of Ni and Fe after the catalytic reaction, suggesting that the studied Ni_1Fe_3 catalyst is stable in water-ethanol solution. Furthermore, catalyst poisoning tests were also performed using various contents of CS_2 (Fig. S16†), where complete poisoning of the Ni_1Fe_3 catalyst was achieved with 0.5 equiv. of CS_2 (as per Ni content in the Ni_1Fe_3 catalyst), further supporting the heterogeneous nature of the studied catalyst.

Deuterium labeling experiments

Deuterium labeling experiments were carried out to determine the source of hydrogen atoms in the alkene product, and to eliminate the direct role of solvent molecules in the observed catalytic activity (Scheme 2).

Initially, the catalytic semihydrogenation of diphenylacetylene (**1a**) was performed over the Ni_1Fe_3 catalyst in (a) D_2O -ethanol (1:1 v/v) and (b) D_2O under the optimized reaction conditions, where deuterated-labeled products were

not observed (Fig. S17 and S18†). However, deuterium incorporation in the alkene/alkane products (as authenticated by ^2D NMR and GC-MS analysis) was only observed, when the reaction was performed using D_2 gas over the Ni_1Fe_3 catalyst in water-ethanol under the optimized reaction conditions (Fig. S19 and S20†). Therefore, the above findings evidenced that the source of hydrogen in the hydrogenated products of alkynes was H_2 gas and not water or ethanol.⁵⁸

Catalyst structure and reaction pathway

It is evident from our experimental findings that the Ni surface is active for the hydrogenation of alkynes, as complete hydrogenation of diphenylacetylene (**1a**) to dibenzyl (**3a**) was achieved over the monometallic Ni catalyst, whereas Fe was found to be inactive. On the other hand, alloying Fe with Ni can significantly tune the alkene selectivity, while maintaining the high catalytic activity for all the bimetallic Ni-Fe catalysts. P-XRD, TEM-EDS line scan, and XPS results indicated the formation of the bimetallic Ni-Fe alloy catalysts, where ICP results authenticated the desired Ni-to-Fe ratio in the synthesized bimetallic Ni-Fe catalysts. Therefore, the observed tuned catalytic activity of the Ni_1Fe_3 catalyst can be associated with the effect of alloying Fe with Ni in Ni/Fe = 1:3, which significantly tuned the properties of the catalyst surface for interaction with alkynes and controlled activation of H_2 molecules. To further investigate the interaction behavior of the catalyst surface with H_2 molecules and to correlate the observed trend with the composition of the bimetallic Ni-Fe catalysts, H_2 -temperature programmed desorption (TPD) experiments over monometallic (Ni and Fe) and bimetallic (Ni_3Fe_1 , Ni_1Fe_1 and Ni_1Fe_3) catalysts were performed and the corresponding H_2 -TPD traces are shown in Fig. S21 and S22.†^{59,60} The H_2 -TPD profile of the monometallic Fe catalyst exhibited a small desorption peak, while that of the monometallic Ni catalyst displayed a prominent hydrogen desorption peak at 371 °C. Therefore, it is clear that the Ni nanoparticle catalyst desorb a greater amount of H-species, indicating a greater capacity of the Ni surface to activate H_2 compared to the Fe catalyst.⁴¹ Further, it is known that H_2 dissociation over the Ni(111) surface is exothermic (−0.75 eV), and hence the availability of abundance of hydrogen atoms over the catalyst surface may result in over-hydrogenation of alkynes to alkanes, which is in good agreement with our experimental results and most of the literature reports.⁴¹ On the other hand, alloying Fe with Ni resulted in significant tuning in the adsorption behavior

Scheme 1 Heterogeneity test of the Ni_1Fe_3 catalyst for the semihydrogenation reaction of **1a**.

Scheme 2 Deuterium labeling experiments for semihydrogenation of diphenylacetylene (**1a**) over the Ni_1Fe_3 catalyst.

of catalyst surfaces. As compared to the monometallic Ni and Fe catalysts, the H_2 -TPD measurements of the bimetallic Ni-Fe catalysts inferred a remarkable shift in the H_2 desorption peak maxima towards the higher temperature region (379–381 °C), suggesting the strong interaction of the bimetallic Ni-Fe with H_2 molecules. As it is clearly seen from the TEM-EDS and XPS results that the bimetallic Ni-Fe alloy catalysts contain Ni and Fe in their alloy composition, the H_2 -TPD results also indicated that in the bimetallic Ni-Fe alloy catalysts the interaction between Ni and Fe significantly tuned the properties of the catalyst active sites, leading to the enhanced interaction of H_2 molecules with the catalyst surface. These observations are also consistent with the trend in the catalytic performance of the bimetallic Ni-Fe catalysts, where all these catalysts having various Ni to Fe ratios exhibited higher catalytic activity for the hydrogenation of diphenylacetylene (**1a**) (Table 1). Notably, in contrast to the bimetallic Ni_1Fe_1 and Ni_3Fe_1 catalysts, the Ni_1Fe_3 catalyst desorbed less hydrogen, but with higher desorption maxima (380 °C). These observations inferred that alloying Fe with Ni not only induced the facile activation of H_2 molecules over the catalyst surface, but also the higher content of Fe in the Ni_1Fe_3 catalyst significantly controlled the adsorption sites on the catalyst surface. Further tuning of the catalyst surface of the bimetallic Ni-Fe catalyst by alloying Fe with Ni in an appropriate composition may greatly influence the interaction of alkenes over the catalyst surface and thus disfavoring over-hydrogenation.^{46,47} Hence, the observed higher catalytic activity of the Ni_1Fe_3 catalyst is not only related to the higher intrinsic activity of Ni, but also to Fe which plays an important role in tuning the adsorption sites of the catalyst surface, as also evidenced by the characterization data and H_2 -TPD experiments, which is considered to be a key factor for the observed higher selectivity for alkenes over the Ni_1Fe_3 catalyst.

Compared to the literature reported non-noble metal based bimetallic Ni-Cu, Ni-Fe and Ni-Co catalysts,^{40,41} the Ni_1Fe_3 catalyst explored in this work displayed high catalytic activity with excellent selectivity for the desired Z-alkene product using a H_2 balloon at 40 °C. Liu *et al.* employed NiCu catalysts for semihydrogenation of internal and terminal alkynes to corresponding alkenes at 65–100 °C in toluene under 4–10 bar H_2 pressure.³⁹ They achieved 81.3% selectivity for stilbene (**2a**) from diphenylacetylene (**1a**) over the NiCu catalyst (pre-NiCu/MMO, MMO = mixed metal oxide) at 80 °C in toluene under 10 bar H_2 pressure. The observed high alkene selectivity over the NiCu catalyst was attributed to easy desorption of alkene over the electron rich Ni surface

resulting from the charge transfer from Cu to Ni. de Vries *et al.* also explored NiFe catalysts along with several bimetallic NiCo and NiCu catalysts and monometallic Ni, Co, Fe and Cu catalysts for the semihydrogenation reaction of 1-octyne in THF under 5 bar H_2 at room temperature.⁴⁰ Their findings inferred that the monometallic Ni and Co nanoparticles were more active towards 1-octyne hydrogenation with 86% and 76% alkene selectivity for the semihydrogenated product as compared to Fe nanoparticles (70% alkene sel.). On the other hand, the Cu catalyst was found to be inactive for the hydrogenation of 1-octyne. Notably, they observed that the bimetallic NiFe (80% alkene sel.) and NiCo (75% alkene sel.) catalysts could not perform well and exhibited catalytic activity analogous to the corresponding monometallic catalysts.⁴⁰ Ternary Cu-Ni-Fe and Cu_3Fe catalysts were also explored for gas-phase hydrogenation of propyne at 250 °C with high alkene selectivity, where the presence of Ni greatly improved the alkene selectivity by disfavoring oligomerization.⁴¹ Compared to these reports, our investigations showed that the monometallic Fe catalyst was inactive, while the Ni catalyst exhibited high activity for the hydrogenation of **1a** but no alkene (**2a**) was observed at 50 °C using a H_2 balloon in water-ethanol solution (Table 1). On the other hand, the bimetallic Ni-Fe catalysts exhibited tuned catalytic performance, where the Ni to Fe ratio in the bimetallic Ni-Fe catalysts significantly influenced the catalytic activity and selectivity towards the semihydrogenated alkene product (**2a**). We observed that Ni_1Fe_3 outperformed the other bimetallic Ni-Fe catalysts and exhibited appreciably good conversion (91%) of **1a** with high selectivity (70%; Z/E 93/7) for the semihydrogenated product Z-stilbene (**2a**) at 50 °C using a H_2 balloon in water-ethanol solution. Moreover, amine additives further improved the selectivity to 91% (Z/E 96/4) for Z-stilbene (**2a**) even at 40 °C with 99% conversion of (**1a**), presumably by disfavoring alkene adsorption and over-

Fig. 4 Schematic representation of the reaction pathway for semihydrogenation of alkynes over Ni-Fe catalysts.

Table 2 Substrate scope of the Ni_1Fe_3 catalyst for semihydrogenation of internal alkynes^a

$$\text{R} \equiv \text{R}' \xrightarrow[\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}, \text{ } n\text{-butyl amine}, \text{ H}_2 \text{ balloon, } 40^\circ\text{C}]{\text{Ni}_1\text{Fe}_3 \text{ catalysts}} \underbrace{\text{R} \text{---} \text{CH=CH} \text{---} \text{R}'}_{\text{2a-2n}} + \underbrace{\text{R} \text{---} \text{CH}_2\text{CH}_2 \text{---} \text{R}'}_{\text{3a-3n}}$$

Entry	Reactants	Products	Time (h)	Conv. ^c (%)	2/3 ^c (%)	Z/E ^c (%)
1	1a		4	99	91/9	96/4
2	1b		6	84	92/8	100/0
3	1c		7	99	87/13	97/3
4	1d		7	95	91/9	100/0
5	1e		10	7	74/26	100/0
6	1f		11	90	96/4	100/0
7	1g		8	99	94/6	93/7
8	1h		12	99	93/7	96/4
9	1i		5	99	98/2	97/3
10	1j		5	99	95/5	100/0
11 ^b	1k		10	57	82/18	100/0
12 ^b	1l		9	19	100/0	100/0
13 ^d	1m		6.5	99	100/0	100/0

Table 2 (continued)

$ \begin{array}{c} \text{R} \equiv \text{R}' \\ \text{1a-1n} \end{array} \xrightarrow[\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}, \text{ } n\text{-butyl amine}, \text{ H}_2 \text{ balloon, } 40^\circ\text{C}]{\text{Ni}_1\text{Fe}_3 \text{ catalysts}} \begin{array}{c} \text{R} \text{---} \text{R}' + \text{R} \text{---} \text{R}' + \text{R} \text{---} \text{R}' \\ \text{2a-2n} \qquad \qquad \text{3a-3n} \end{array} $						
Entry	Reactants	Products	Time (h)	Conv. ^c (%)	2/3 ^c (%)	Z/E ^c (%)
14 ^d			4	99	95/5	100/0
	1n					

^a Reaction conditions: alkyne (1.0 mmol), catalyst (10 mol%), *n*-butyl amine (0.55 mmol), water-ethanol (20 mL, 1:1 v/v), 40 °C. ^b Alkyne (0.5 mmol), catalyst (20 mol%), *n*-butyl amine (0.55 mmol), water-ethanol (20 mL, 1:1 v/v), 40 °C. ^c Conversion of the substrate and selectivity of (*Z*) *cis*-alkene, (*E*) *trans*-alkene and alkane was determined by ¹H NMR. ^d Conversion of the substrate and selectivity of (*Z*) *cis*-alkene, (*E*) *trans*-alkene and alkane was determined by GC.

hydrogenation due to relatively high adsorption behavior of amine additives as compared to the alkene product. Hence, based on our experimental findings and the available precedent reports,⁵⁸ it is evident that presumably the homolytic dissociation of H₂ gas initially occurred over the catalyst surface, which was followed by the concerted transfer of hydrogen atoms from the catalyst surface to the adsorbed alkynes leading to the formation of the *Z*-alkene products. A schematic representation of the reaction pathway for alkene dehydrogenation is shown in Fig. 4.

Substrate generality for semihydrogenation of alkynes

To expand the scope and generality of the highly active Ni₁Fe₃ catalyst, we further investigated catalytic semihydrogenation of a wide range of internal alkynes (**1a–1n**) under the optimized reaction conditions in water-ethanol solution at 40 °C, where high selectivity towards the respective *Z*-alkene products was achieved (Table 2, entries 1–12). When *para*-substituted diaryl alkynes (**1b** and **1c**) were used, the reaction proceeded well to yield the respective alkenes with high selectivity (*Z*/*E* 100/0 (**2b**) and 97/3 (**2c**)) (Table 2, entries 2–3). Notably, the sterically hindered *meta*-dimethyl substituted diphenylacetylene (**1d**) was also selectively hydrogenated to an alkene (**2d**) (**2d/3d** 91/9, *Z*/*E*: 100/0) with good conversion (95%) (Table 2, entry 4). On the other hand, with the diphenylacetylene substrate (**1e**) having an amide group at the *para* position poor conversion was observed, attributed to the weak adsorption of the triple bond over the catalyst surface (Table 2, entry 5).⁶¹ Analogous to diphenylacetylene, aryl-alkyl alkynes (**1f–1j**) were also effectively hydrogenated to their corresponding alkene products (**2f–2j**) with excellent selectivity for the *Z*-alkenes (*Z*/*E* 93/7–100/0). The hydroxyl substituted internal alkyne (**1f**) was hydrogenated to the corresponding *Z*-alkene (**2f**) with good conversion (90%) and high selectivity for the corresponding *Z*-alkene (*Z*/*E* 100/0), but the reaction was a little sluggish (Table 2, entry 6).⁶² Moreover, the more sterically hindered hydroxyl substituted internal alkynes **1g**

and **1h** were also successfully hydrogenated to *Z*-alkenes (*Z*/*E* 93/7 (**2g**) and 96/4 (**2h**) with high conversion (99%) (Table 2, entries 7–8). The observed high selectivity for *Z*-alkenes with sterically bulky hydroxyl substituted internal alkynes was probably due to the weak interaction of the alcohol group with the catalyst surface which retarded the over reduction of alkenes (**2g** and **2h**) to alkanes (**3g** and **3h**). Moreover, semihydrogenation of alkyl-aryl alkynes with substituted (**1i**) and unsubstituted (**1j**) aliphatic chains also proceeded well to their corresponding *Z*-alkene products with good selectivity (*Z*/*E* 97/3 (**2i**) and 100/0 (**2j**)) and high conversion (99%) (Table 2, entries 9–10). Furthermore, we also explored the Ni₁Fe₃ catalyst for the hydrogenation of bi(hetero)aryl alkynes (**1k** and **1l**), albeit a lower conversion of alkynes to their corresponding alkene (**2k** and **2l**) products was observed, which can be associated with the strong interactions of the heteroatoms (S and N) with the catalyst surface (Table 2, entries 11 and 12). Nevertheless, a higher selectivity of 83% (**2k**) and 100% (**2l**) with complete selectivity for *Z*-alkene products was achieved over the Ni₁Fe₃ catalyst. Moreover, aliphatic internal alkynes, 3-hexyn-2-ol (**1m**) and 5-decyne (**1n**) can also be successfully hydrogenated to *Z*-alkenes with very good selectivity (Table 2, entries 13 and 14). Apart from the internal alkynes, the Ni₁Fe₃ catalyst was also subjected for the hydrogenation of terminal alkynes, where only totally hydrogenated products were observed (Scheme S1†). Moreover, for practical application, we synthesized the catalyst on a higher scale (10 times higher than the small-scale synthesis) and investigated its catalytic activity under the optimized reaction conditions. The results inferred that the activity and selectivity of the synthesized Ni₁Fe₃ catalyst for the semihydrogenation of **1a** to *Z*-stilbene (**2a**) do not change (Table S2†). Furthermore, the TEM image of the synthesized catalysts at a higher scale shows the presence of nanoparticles with an average particle size of *ca.* ~6.0 nm (Fig. S23†), which is consistent with the particle size (*ca.* ~6.5 nm) for the Ni₁Fe₃ catalyst synthesized on a small scale (Fig. 1 and S4†).

Experimental

Syntheses of the Ni_1Fe_1 , Ni_3Fe_1 and Ni_1Fe_3 catalysts

The bimetallic Ni–Fe catalysts with various Ni/Fe molar ratios were synthesized using the polyvinylpyrrolidone (PVP) stabilized aqueous phase co-reduction process.⁴⁷ Typically, 0.012 g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and 0.042 g of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 5 mL of distilled water containing 0.100 g of PVP and sonicated for 5 min. An aqueous solution of sodium borohydride (5 mL, 0.050 g) was added dropwise to the above mixture and sonicated again for 5 min to obtain a black suspension of the Ni_1Fe_3 catalyst, which was magnetically separated and washed with a copious amount of deionized water and ethanol under inert gas protection in a Schlenk line. Analogously, the Ni_1Fe_1 and Ni_3Fe_1 catalysts were synthesized using appropriate amounts of Ni^{+2} and Fe^{+2} precursors in the specified molar ratio. Moreover, the monometallic Ni and Fe catalysts were also synthesized following an analogous synthetic procedure. It should be noted that all the catalysts were magnetically separated except the Ni catalyst, which was separated by centrifugation (5000 rpm for 10 min). The XPS survey analyses of the synthesized catalysts (Fig. S24–S28) show the presence of prominent peaks of the desired elements, suggesting that the synthesized catalysts are free from impurities such as metal salts or other by-products.

Catalytic semihydrogenation of alkynes

A reaction flask was charged with the freshly prepared catalyst (10 mol%) dispersed in water/ethanol (20 mL, 1:1 v/v), and was purged with N_2 gas. After that, alkynes (1.0 mmol) and *n*-butyl amine (0.55 mmol) were added in the solution and the reaction mixture was stirred at 40 °C equipped with a H_2 balloon. After completion of the reaction, the catalyst was magnetically separated from the reaction mixture. The reaction mixture was extracted with dichloromethane (3×5 mL), and the combined organic layer was dried in anhydrous Na_2SO_4 , filtered, and concentrated under reduced pressure. The products were characterized by ^1H NMR, ^{13}C NMR and GC-MS.

Conclusion

We synthesized bimetallic Ni–Fe catalysts and explored these catalysts for the catalytic semihydrogenation of internal alkynes to *Z*-alkenes under moderate reaction conditions. All the monometallic (Ni and Fe) and bimetallic Ni–Fe catalysts were extensively characterized to establish their morphology, chemical nature and adsorption sites using HR-TEM, SEM, XPS, EDS point and line scan, PXRD and H_2 -TPD measurements. Results inferred that the catalytic activity of the studied bimetallic Ni–Fe catalysts was significantly governed by the Ni-to-Fe ratio, where the Ni_1Fe_3 catalyst exhibited superior catalytic activity for the semihydrogenation of alkenes with high diastereoselectivity for *Z*-alkenes. Notably, significantly distinct catalytic performance of the bimetallic Ni–Fe catalysts as compared to the monometallic

Ni and Fe catalysts was observed suggesting the crucial role of alloying Fe with Ni in achieving superior catalytic performance of the bimetallic Ni–Fe catalyst. H_2 -TPD results inferred that alloying Fe with Ni not only induced the facile activation of H_2 molecules over the catalyst surface, but also the higher content of Fe in the Ni_1Fe_3 catalyst significantly controlled the adsorption sites on the catalyst surface. Moreover, we emphasized the role of amine-based additives to substantially enhance the alkene selectivity, and found that *n*-butyl amine accelerated alkene selectivity by disfavoring over-hydrogenation of alkynes to *Z*-alkanes. Hence, the generality and scope of the high performance Ni_1Fe_3 catalyst were explored for the catalytic hydrogenation of a wide range of internal alkynes to their respective alkenes wherein significantly high selectivity for *Z*-alkene was achieved. Advantageously, the bimetallic Ni–Fe catalysts can be easily recovered using an external magnet after the catalytic reaction. Furthermore, deuterium labeling experiments using D_2 and D_2O revealed that the source of hydrogen in alkenes is H_2 gas, and not water or ethanol. It is worth mentioning here that the studied Ni_1Fe_3 catalyst exhibited excellent stability in water–ethanol solvent, as confirmed by ICP, TEM and XPS. We believe that the synthesized bimetallic Ni–Fe catalysts represent a class of magnetically recoverable low-cost high-performance non-noble metal-based catalysts which can open new ways to the scientific community for exploring such catalysts for various other industrially important reactions.

Conflicts of interest

Acknowledgements

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