Supporting Information

Fe hotspots in Ni-Ni_3B nanocatalyst unravel remarkable cooperativity to boost hydrogen production from ammonia borane with enzyme-like catalysis

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1. Materials and methods

1.1 Chemicals and materials

Methanol (HPLC gradient grade, S. D. Fine Chemicals Pvt. Ltd.), Ferric nitrate LR ($Fe(NO_3)_3.9H_2O$, S. D. Fine Chemicals Pvt. Ltd.), Nickel nitrate extrapure ($Ni(NO_3)_2.6H_2O$, S. D. Fine Chemicals Pvt. Ltd.), Dopamine hydrochloride (Sigma Aldrich), Milli-Q water were used as received. Ammonia borane (AB) was synthesized using Ammonium sulphate extrapure AR grade (Sisco Research Laboratories Pvt. Ltd.) and Sodium borohydride extrapure (Sisco Research Laboratories Pvt. Ltd.) in Tetrahydrofuran (HPLC grade, S. D. Fine Chemicals Pvt. Ltd.) by following the procedure described by Ramachandran and Gagare.[1]

1.2. Synthetic methods

Synthesis of Ni-Ni_3B and (5, 10, 25, 50, 75) % Fe-Ni-Ni_3B catalysts

In the Schlenk tube containing 2 mL methanol, 0.1, 0.095, 0.09, 0.075, 0.05, 0.025 mmol of $Ni(NO_3)_2.6H_2O$ and 0, 0.005, 0.01, 0.025, 0.05, 0.075 mmol of $Fe(NO_3)_3.9H_2O$ were added, respectively, to prepare Ni-Ni_3B and 5, 10, 25, 50, 75 % Fe-Ni-Ni_3B catalysts. To this solution, an excess of AB was added while sonicating till the formation of black precipitate with the evolution of gas bubbles. 5, 10, 25, 50, 75 % Fe-Ni-Ni_3B catalysts were separated using a magnet, crushed with a glass rod, and were washed twice with methanol, and were used further for the dehydrogenation catalysis. Ni-Ni_3B is weakly magnetic. Hence, it was allowed to settle during separation and carefully washed with methanol, and used further.

1.3. Characterization

UV-Visible spectra were recorded on Shimadzu UV-1800 UV spectrophotometer, scanning electron microscopy (SEM) imaging and X-ray mapping was performed on Zeiss microscope and FEI Apreo microscope. Powder XRD analysis was performed on Bruker X-ray diffractometer (Cu Kα 1.5406 Å radiation). X-ray photoelectron spectroscopy (XPS) was recorded on a MULTLAB 2000 THERMO SCIENTIFIC, UK. Transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) patterns were recorded on the JEOL (JEM 2100 Plus electron microscope) after drop-casting dispersion of nanocatalyst in MeOH over Copper TEM grid. NMR experiments were performed using Bruker Ascend 400 MHz spectrometer. Multiple point BET surface areas and pore structures were measured with a surface area and porosity analyzer (Micromeritics Tristar 3000, USA), at the temperature of liquid nitrogen. Before the analysis, samples were degassed at 200 °C for 8 h with a continuous flow of nitrogen gas. Magnetic properties were studied as a function of the applied field (M–H) using a vibrating sample magnetometer (VSM) on a Quantum Design-Versa Lab model.

1.4. H_2 generation experiments

1.4.1. Dehydrogenation of AB

1 mL 0.5 M AB solution was taken in a 1 mL syringe and was injected, while stirring, into the Schlenk tube (containing catalyst) placed in a water bath maintained at room temperature. The volume of gas evolved per unit time was measured by recording the volume of water displaced from the burette. The final volume of the H_2 gas generated was found out by equalizing the level of the water in the reservoir with the level of the water in the gas burette. The experiments were done in triplicate sets and the graphs were plotted using the Origin software.

1.4.2. Variation of Fe concentration in Ni-Ni_3B for dehydrogenation of AB

The catalytic activities of the prepared Ni-Ni_3B and 5, 10, 25, 50, 75 % Fe-Ni-Ni_3B catalysts were studied for dehydrogenation of AB according to the procedure (1.4.1). The experiments were conducted in triplicate and the rate and TOF was calculated for each catalyst.

1.4.3. Variation of the amount of catalyst (10% Fe-Ni-Ni_3B) for dehydrogenation of AB

0.5, 1, 1.5, 2, 2.5 times 10% Fe-Ni-Ni_3B catalysts were synthesized and tested for AB dehydrogenation activity by adding 1 mL of 0.5 M AB solution separately to the Schlenk tube. The gas generated was measured according to procedure (1.4.1). The experiments were conducted in triplicate and the rate for each reaction was calculated.

1.4.4. Dehydrogenation of AB using 10% Fe-Ni-Ni_3B by temperature variation

10% Fe-Ni-Ni_3B was synthesized in the Schlenk tube and its catalytic activity was checked at 283, 293, 303, 313, and 323 K according to procedure (1.4.1). The experiments were conducted in triplicate and the rate for each reaction was calculated.

1.4.5. Variation of AB concentration using 10% Fe-Ni-Ni_3B for dehydrogenation of AB

10% Fe-Ni-Ni_3B was synthesized in the Schlenk tube and its catalytic activity was checked by adding 1 mL of 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875 and 1 M AB solution according to procedure (1.4.1). The experiments were conducted in triplicate and the rate for each reaction was calculated.

1.4.6. Reusability test of 10% Fe-Ni-Ni_3B for dehydrogenation of AB

After using 10% Fe-Ni-Ni_3B once for AB dehydrogenation, it was separated with the help of a magnet and the supernatant clear solution was discarded. The used catalyst was washed once with methanol and it was reused for AB dehydrogenation according to the procedure (1.4.1).

Similarly, the activity of the catalyst was checked for 12 consecutive catalytic cycles and the rate for each cycle was calculated.

1.4.7. AB dehydrogenation by 10% Fe-Ni-Ni_3B in the presence of dopamine hydrochloride

To the Schlenk tube containing synthesized 10% Fe-Ni-Ni_3B catalyst, 500 µL of 0.5 M dopamine hydrochloride solution was added and was sonicated for ~1 min. To it, 500 µL of 1 M AB solution was added and the activity was tested following the aforementioned procedure (1.4.1).

1.4.8. Testing AB dehydrogenation by 10% Fe-Ni-Ni_3B prepared using Fe(II) salt

The catalyst was prepared using the previously mentioned procedure but using 10 % Fe(II) salt in place of Fe(III) salt and the dehydrogenation activity was checked using the aforementioned procedure (1.4.1)

Calculation of turnover frequency (TOF)

The turnover frequency (TOF) was calculated by the following formula.

$$\text{TOF} = \frac{(\text{moles of } H_2 \text{ generated})}{(\text{moles of catalyst})\,(\text{time})}$$

2. Supplementary figures and tables

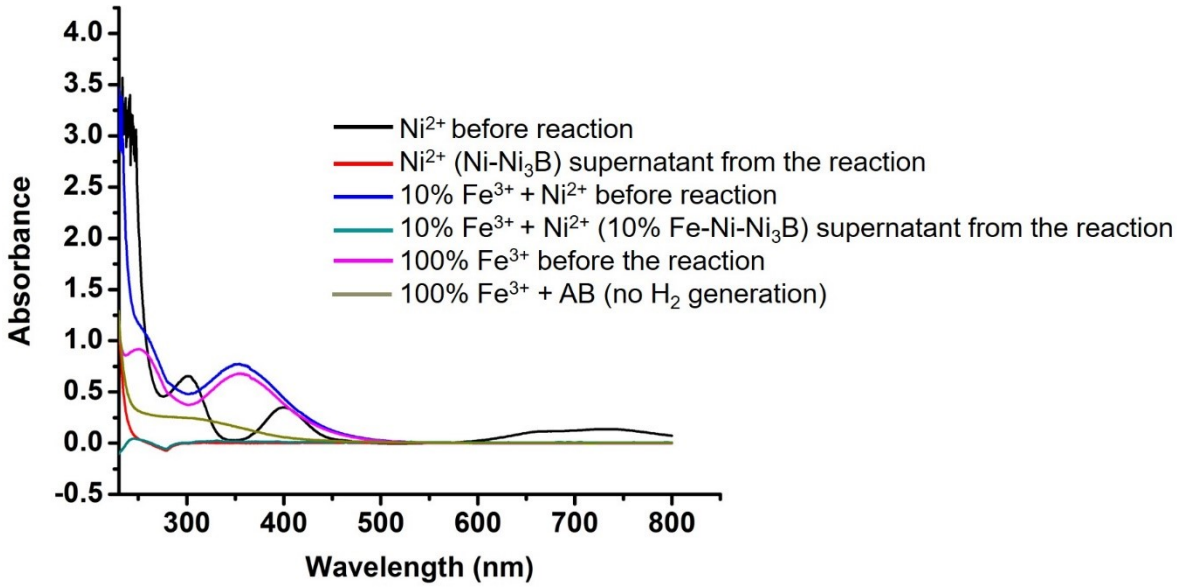

Figure S1. UV-Vis spectra of the reactions carried out under following conditions.

Conditions:

Black line: Spectrum of 50 mM Ni^{2+} solution

Red line: Spectrum of supernatant obtained after the reaction of 50 mM Ni^{2+} and an excess of AB

Blue line: Spectrum of the mixture containing 2.25 mM Ni^{2+} and 0.25 mM Fe^{3+} (The stock mixture was diluted 20 times as the absorbance of crossing value of 1)

Green line: Spectrum of supernatant obtained after the reaction of 45 mM Ni^{2+} and 5 mM Fe^{3+} and an excess of AB

Pink Line: Spectrum of 0.25 mM Fe^{3+} solution (diluted 200 times from the stock solution of 50 mM Fe^{3+})

Dark yellow line: Spectrum of 0.25 Fe^{3+} solution containing excess of AB (diluted 200 times from the stock solution of 50 mM Fe^{3+}, no reduction of Fe^{3+} to Fe^{0} was observed, although there was a shift in the peak from 350 nm to 330 nm)

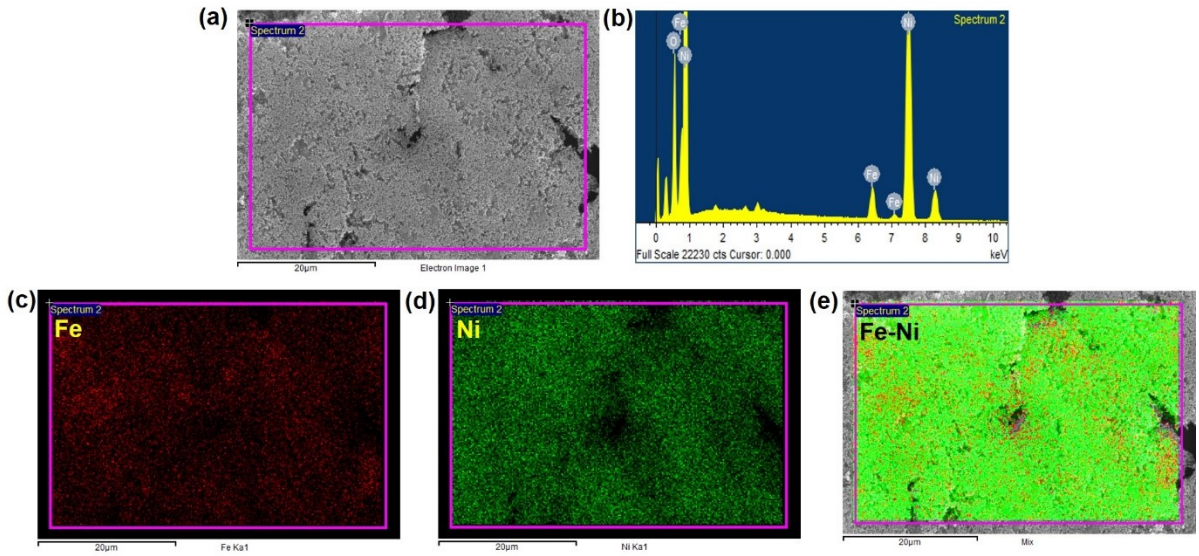

Figure S2. (a) SEM image of 10% Fe-Ni-Ni_3B. The marking indicates the area probed for recording EDX spectra, (b) EDX spectra of 10% Fe-Ni-Ni_3B, (c-e) X-ray map of Fe, Ni and Fe-Ni together, respectively.

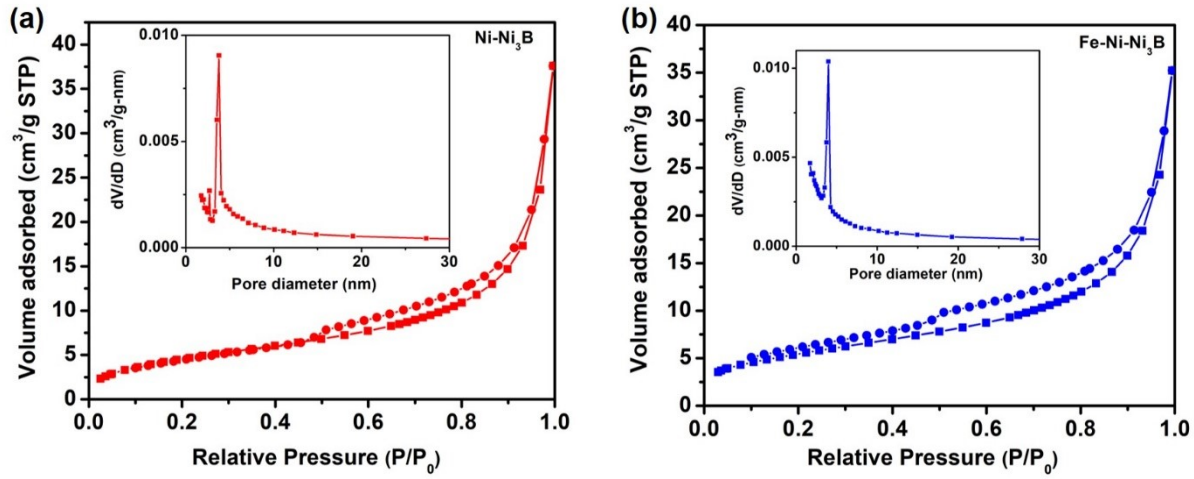

Figure S3. BET adsorption isotherm for (a) Ni-Ni_3B, (b) 10% Fe-Ni-Ni_3B.

Table S1. The comparative parameters obtained from BET surface area measurement of Ni-Ni_3B and 10% Fe-Ni-Ni_3B nanocatalysts.

Sample No	BET Surface Area (m^2/g)	BJH Desorption cumulative surface area of pores (m^2/g)	BJH Desorption cumulative volume of pores (cm^3/g)	BJH Desorption average pore diameter (nm)
Ni-Ni_3B	17.2556	19.6447	0.057998	11.8094
10% Fe-Ni-Ni_3B	19.6502	24.6560	0.055684	9.0338

Table S2. The parameters obtained from the *M-H* curves of 10% Fe-Ni-Ni_3B nanocatalyst.

Temperature (K)	Highest magnetization at 3T (emu g^{-1}) M_s	Remanance magnetization (emu g^{-1}) M_r	Coercivity (Oe)
300	7.05	0.29	4.99
50	15.15	2.68	146.30

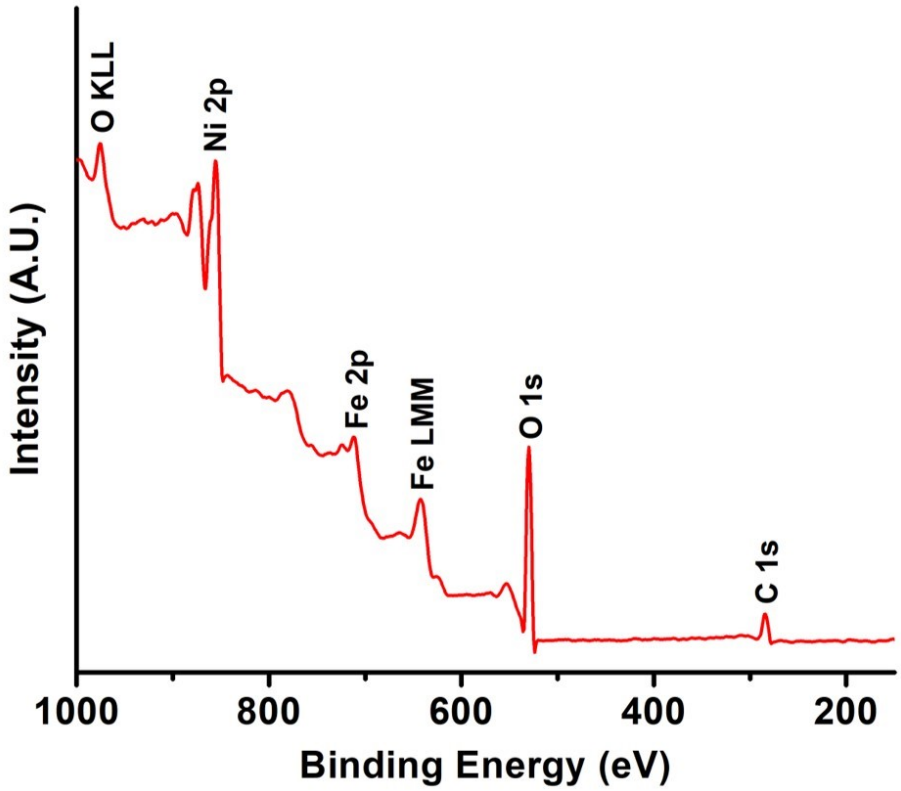

Figure S4. Survey XPS of 10% Fe-Ni-Ni_3B nanocatalyst.

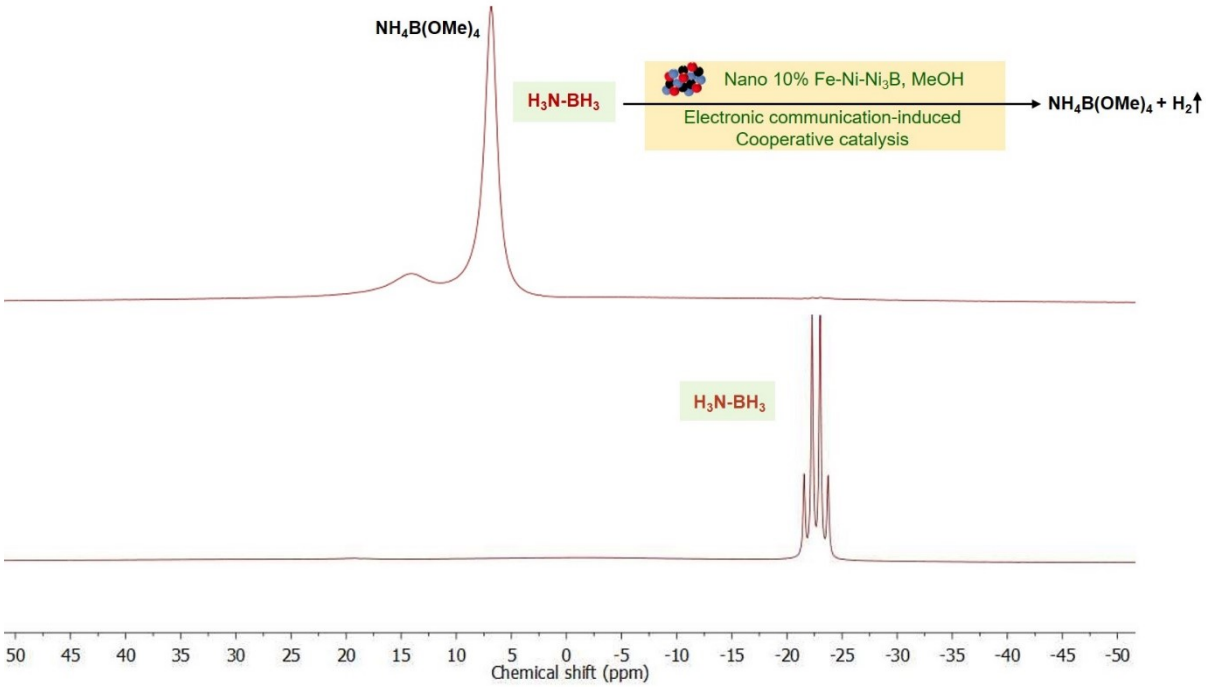

Figure S5. ^{11}B NMR spectra of (a) AB and (b) supernatant obtained after the AB dehydrogenation reaction.

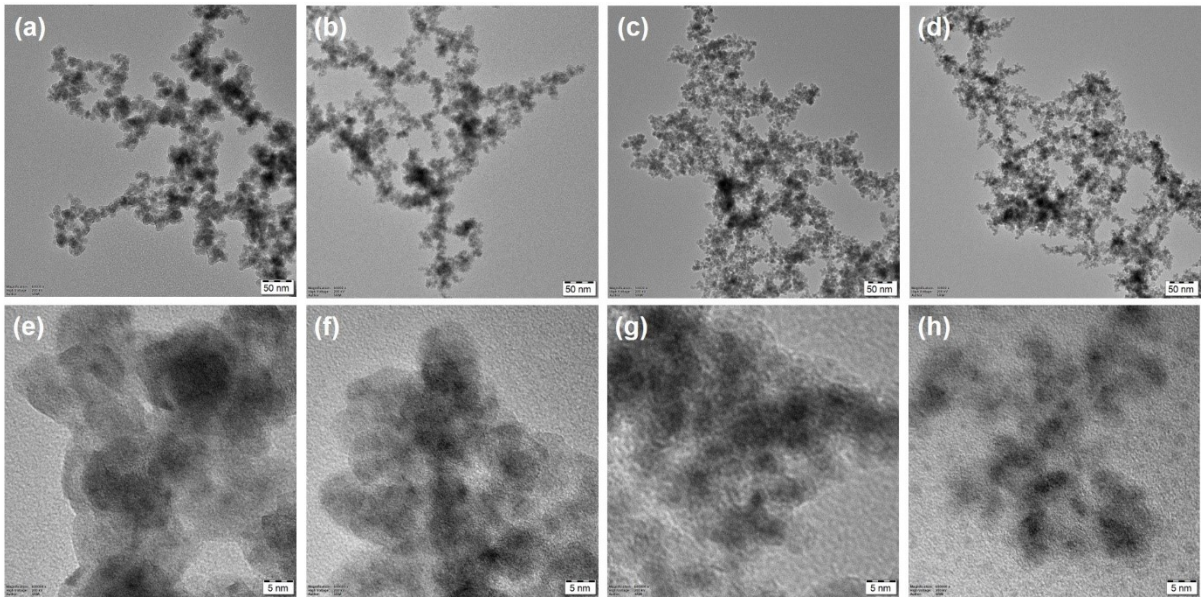

Figure S6. TEM and HRTEM images of (a and e) Ni-Ni_3B, (b and f) 5% Fe-Ni-Ni_3B, (c and g) 10% Fe-Ni-Ni_3B, and (d and h) 25% Fe-Ni-Ni_3B, respectively.

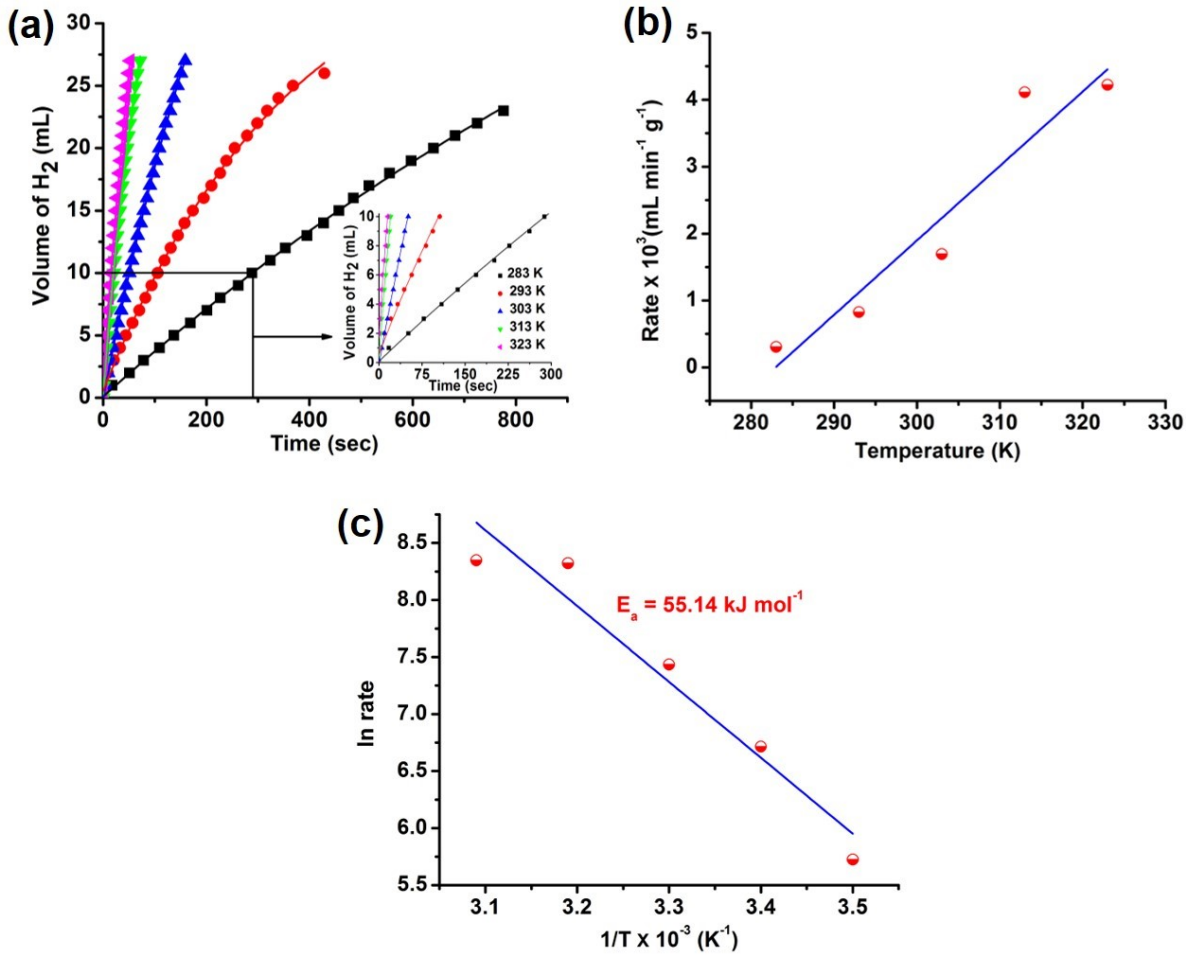

Figure S7. (a) Effect of temperature on the AB dehydrogenation reaction catalyzed by Ni-Ni_3B nanocatalyst, (b) Plot of rate vs temperature, (c) Arrhenius plot showing the E_a value of 55.14 kJ mol^{-1} for the AB dehydrogenation reaction catalyzed by Ni-Ni_3B nanocatalyst.

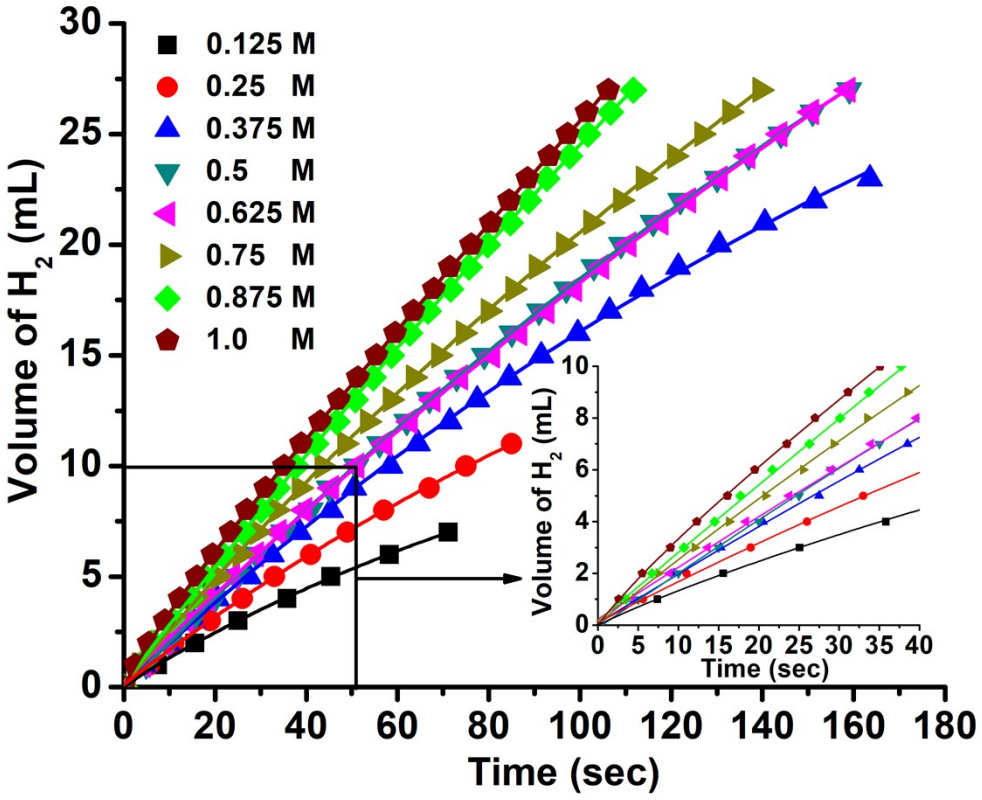

Figure S8. Effect of AB concentration on the rate of dehydrogenation of AB catalyzed by Ni-Ni_3B nanocatalyst.

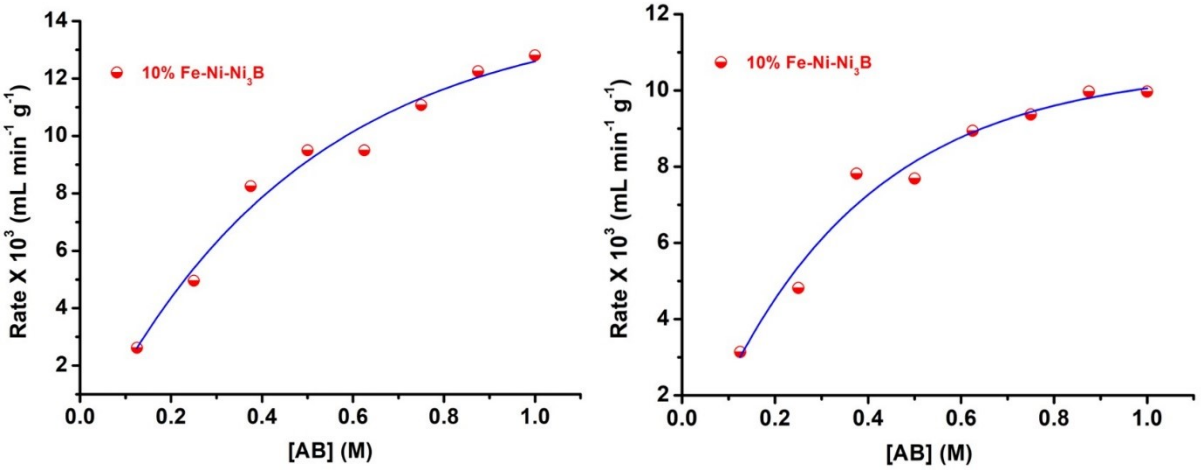

Figure S9. Duplicates of Michaelis-Menten plots for dehydrogenation of AB catalyzed by 10 % Fe-Ni-Ni_3B nanocatalyst.

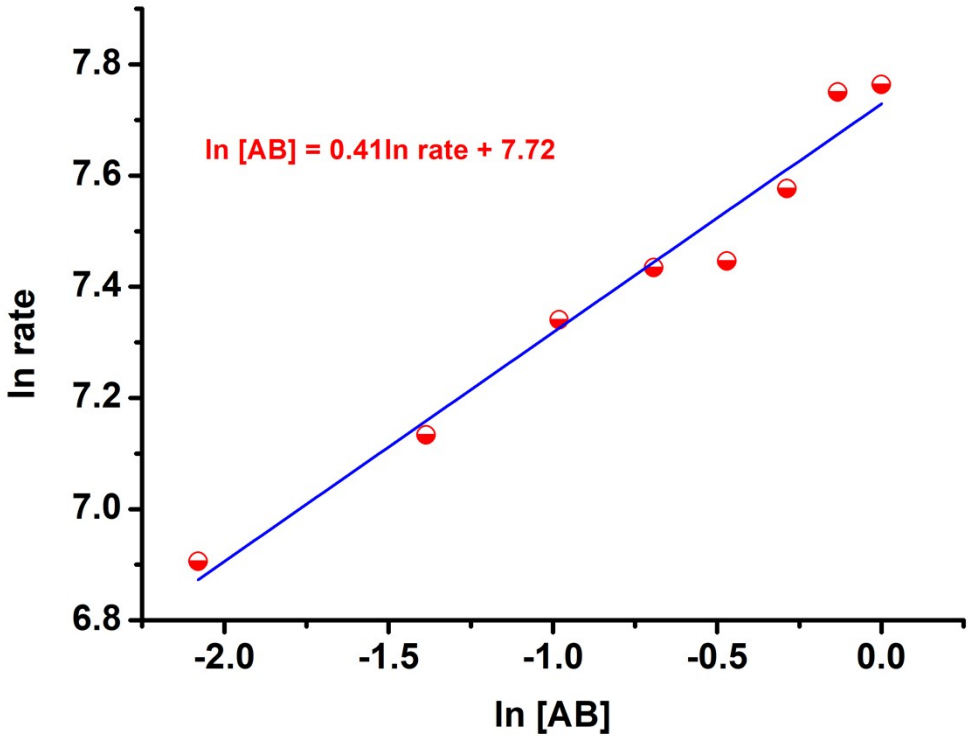

Figure S10. Plot of ln rate v/s ln [AB] showing half order kinetics of the AB dehydrogenation reaction catalyzed by Ni-Ni_3B nanocatalyst.

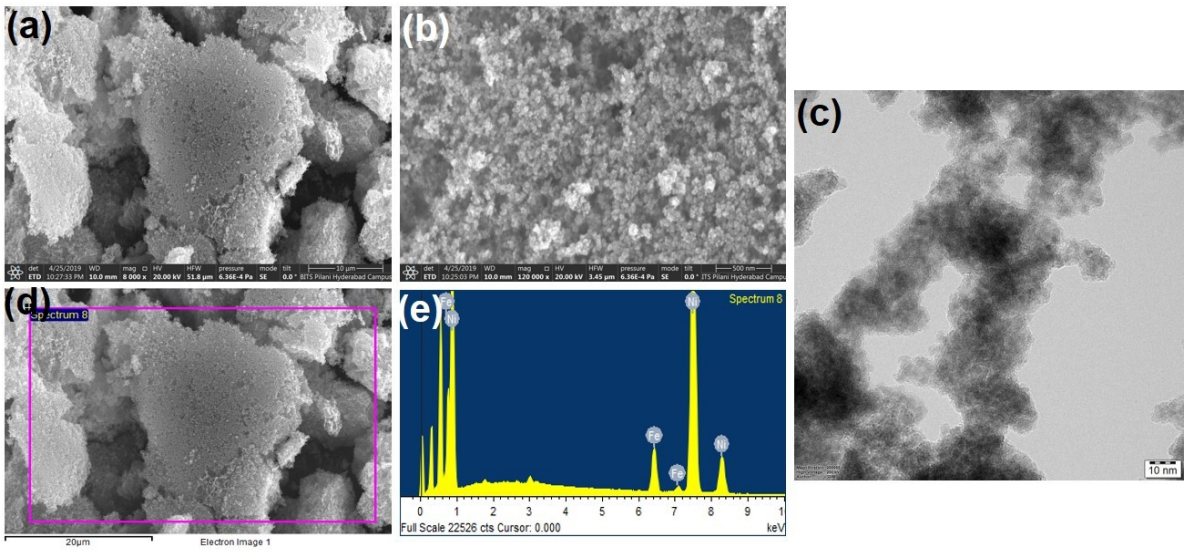

Figure S11. (a-c) SEM image, High resolution SEM image and TEM image, respectively, of the reused 10% Fe-Ni-Ni_3B nanocatalyst, (d) The marked area of the SEM image of reused 10% Fe-Ni-Ni_3B nanocatalyst to probe the elemental species by EDX, (e) EDX spectrum of the reused 10% Fe-Ni-Ni_3B nanocatalyst.

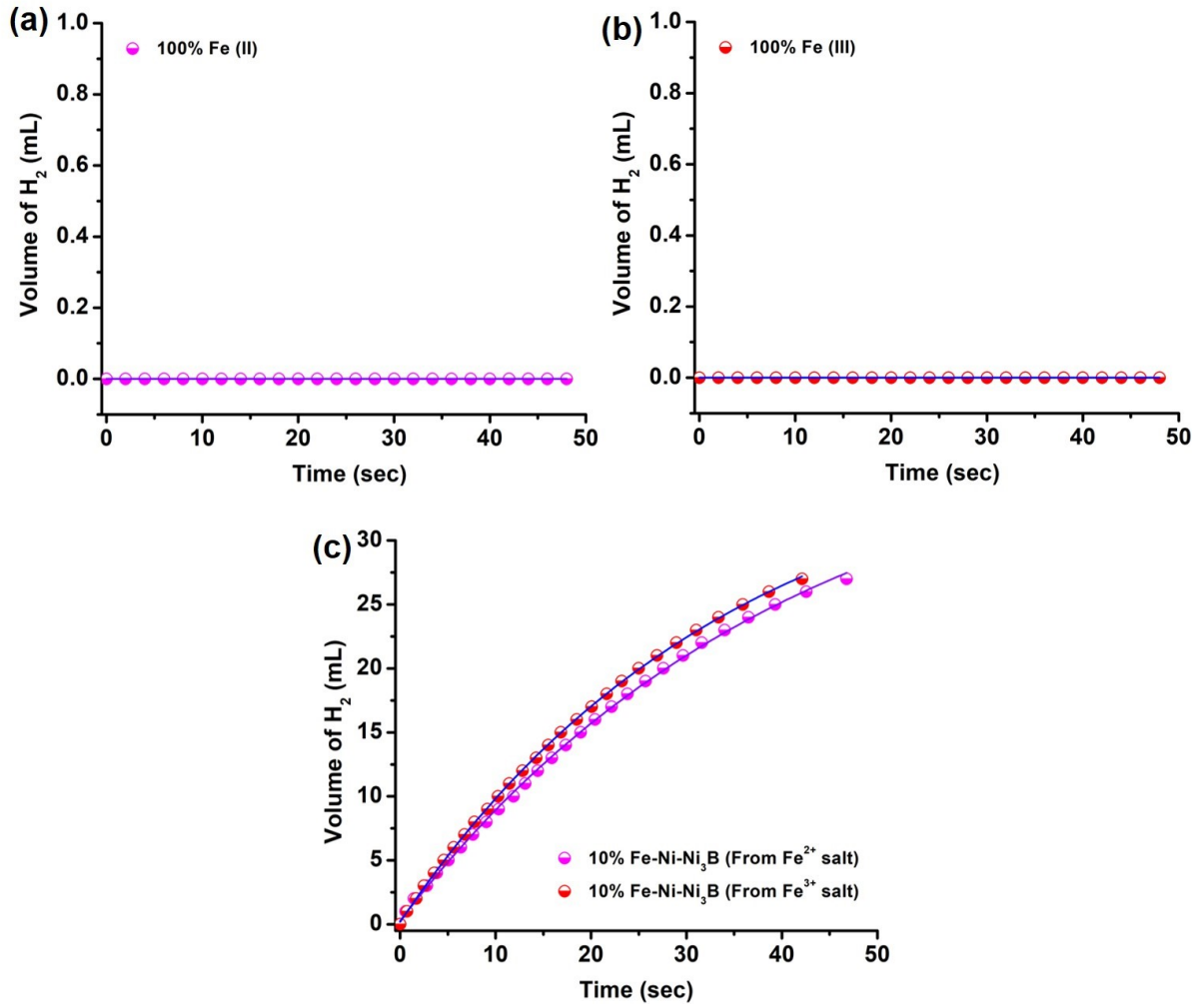

Figure S12. A test for AB dehydrogenation activities using (a) Fe(II) and (b) Fe(III) ions (0.1 mmol, 100 %), (c) 10% Fe-Ni-Ni_3B prepared from Fe(II) and Fe(III) ions.

Table S3. Comparison of TOF, E_a and type of kinetics shown by some Ni-based catalysts for AB dehydrogenation reaction.

Catalysts	TOF (min^{-1})	*Ea* (kJ mol^{-1})	Kinetics	Ref.
PVP-stabilized Ni^0 nanoparticles	12.1	62± 2	Zero-order	[2]
Nanoporous Ni spheres	19.6	27 ± 1	Near zero-order	[3]
CVD-Ni/ZIF-8	14.2	-	-	[4]
CLD-Ni/ZIF-8	8.4	-	-	[4]
$Ni_{1.2}Fe_{0.8}$@CN-G	23.25	36.83	First-order	[5]
Ni/BN	1.03	63.2	-	[6]
Ni/SiO_2	13.2	34 ± 2	Half-order	[7]
Ni^0 /CeO_2	1.7	25	-	[8]
Ni/g-C_3N_4	18.7	36	Zero-order	[9]
Ni/KB	7.47	-	Zero-order	[10]

Ni/C	8.8	28 ± 2	Zero-order	[11]
Ni/CNT	26.2	32.3	-	[12]
10% Fe-Ni-Ni_3B	29.33	39.95	Michaelis- Menten	This work

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