

## Supporting Information

# Unraveling High Alkene Selectivity at Full Conversion in Alkyne Hydrogenation over Ni under Continuous Flow Conditions

### Table of Contents

<b>1. General information</b>	<b>1</b>
<b>2. Synthesis methods</b>	<b>2-3</b>
<b>3. Characterization of derived nickel nanoparticles</b>	<b>3-5</b>
<b>4. Catalysis: Semi-Hydrogenation of phenylacetylene under fixed bed down flow reactor</b>	<b>5-16</b>
<b>5. Characterization of spent catalyst</b>	<b>17</b>
<b>6. Semi-hydrogenation of alkynes in a batch reactor</b>	<b>17-18</b>
<b>7. Literature</b>	<b>18</b>

### 1. General information

#### 1.1. Reagents

Phenyl acetylene (99%), styrene (99%) were purchased from Sigma-Aldrich. 2, 5-dihydroxyterephthalic acid (H<sub>4</sub>DOBDC, > 98.0 %) was brought from TCI, Chennai, India. Nickel nitrate hexahydrate (Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, 99%) was purchased from Merck Life Science Pvt. Ltd. Mumbai, India. Ethylbenzene (99%) was purchased from Spectrochem Pvt. Ltd, Mumbai, India. N, N-dimethylformamide (DMF, 99 wt %), and Methanol (98.0 %) were purchased from Avra Synthesis Pvt. Ltd. Hyderabad, India. All chemicals were used without further purification.

#### 1.2. Characterization

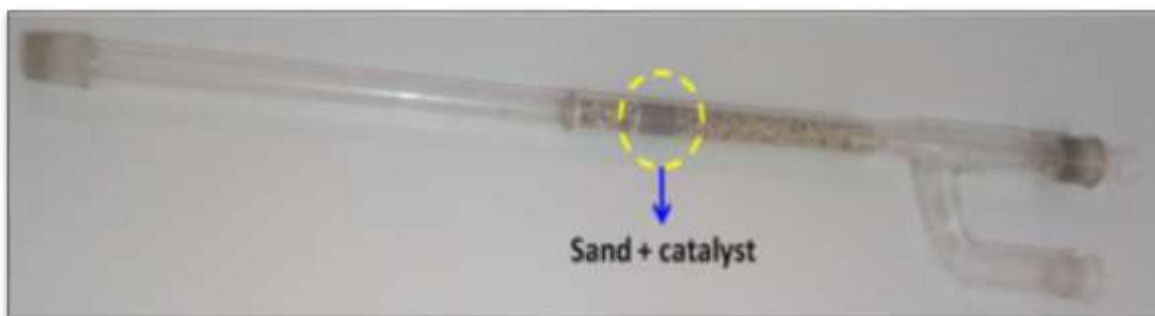
Powder X-ray diffraction (PXRD) patterns were recorded on Bruker with Cu K<sub>α</sub> radiation ( $\lambda = 1.5418 \text{ \AA}$ ) operating at 20 kV and 10 mA. The specific surface area, pore volume, and pore size of catalysts were measured using a BEL Corp II BET (Brunauer-Emmett-Teller) instrument. Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) imaging were carried out using JEOL 2100F, FEG source, 200 kV source voltage Oxford EDS detector. The Ni

content sample was determined by the ICP-OES Varian 720-ES instrument. Temperature programmed Desorption (TPR), BELCAT II (Japan) with TCD detector.

## 2. Synthesis of MOF-74(Ni)

MOF-74(Ni) has been synthesized as per the literature procedure.<sup>1</sup> In a typical synthesis, 2, 5-dihydroxyterephthalic acid ( $H_4DOBDC$ , 0.478 g, 2.41 mmol) and  $Ni(NO_3)_2 \cdot 6H_2O$  (2.378 g, 8.178 mmol) precursors were dissolved in 200 mL of 1:1:1 (v/v/v) mixture of DMF–ethanol– $H_2O$  and transferred into a 500 mL screw-capped bottle. The mixture was sonicated until it became homogeneous and placed in a preheated oven at 100 °C for 24 hours. After completion of the reaction time, the reaction mixture was brought to room temperature and the mother liquor was isolated from the yellow precipitate. Then, the precipitate was washed with methanol three times and finally, it was dried under vacuum at room temperature.

### 2.1. Synthesis of Ni@C materials from MOF-74 in a fixed bed reactor



**Figure S1:** Fixed bed reactor loaded with MOF-74(Ni) material with the dilution of sand (circle).

In a typical procedure, 0.175 g of MOF-74(Ni) was uniformly distributed in 4 g of sand and was placed in a quartz reactor tube (I.D. = 11 mm, O.D = 16 mm) which was placed between silica wool as indicated in the circle (figure S1). A thermo vial (containing thermocouples) was inserted on the top of the silica wool to monitor the bed temperature. Then the quartz reactor surrounded by a vertical furnace was connected in between a pre-heater and a water condenser. The temperature of the sample was slowly raised to 330 °C under  $N_2$  flow (20 mL/min) and maintained at that temperature for 3h. After pyrolysis, the bed temperature was brought to room temperature. The material was further treated with  $H_2$  flow (20 mL/min) for 3 h at three different temperatures 120 °, 200 °C, and 300 °C. The materials were labeled as Ni@C-120R, Ni@C-200R, and Ni@C-300R, respectively. The yield of materials was ~102 mg. For analysis purposes, the reduced material was isolated from sand and characterized using different techniques.

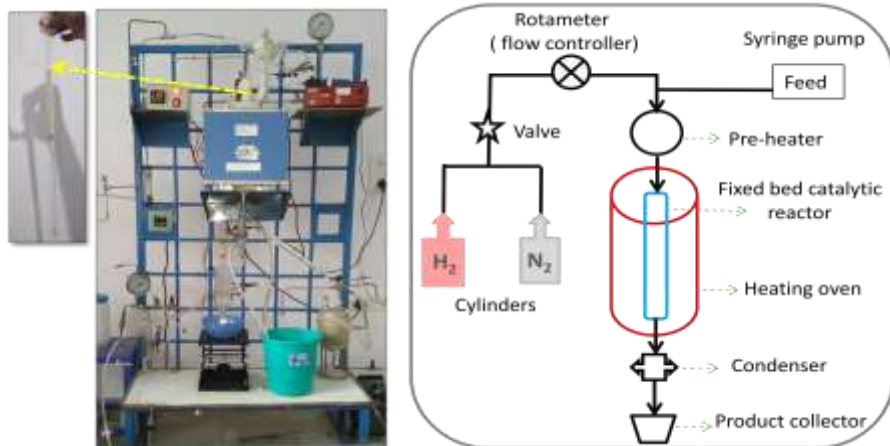


Figure S2: Schematic representation of a fixed bed continuous flow reactor.

### 3. Characterization of derived nickel nanoparticles

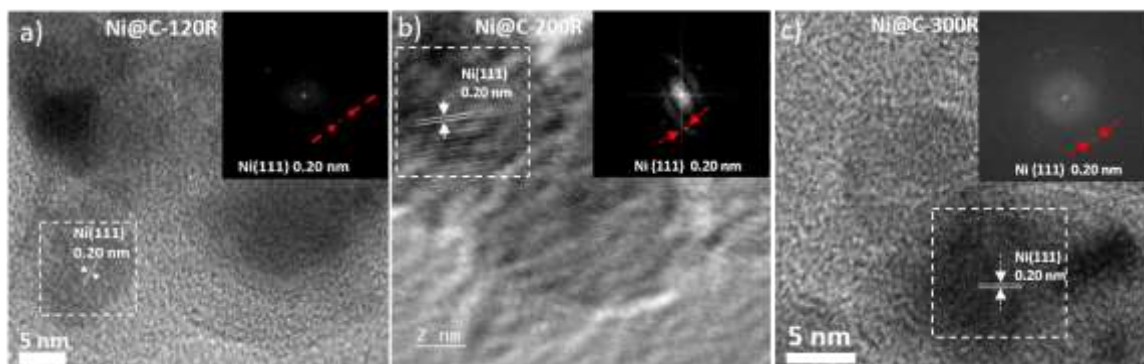


Figure S3: High resolution-TEM and FFT plots of Ni@C-120R, Ni@C-200R, and Ni@C-300R materials. (In the FFT plot, the corresponding plane of (111) belongs to the Ni FCC crystal structure). We did not observe formation of Ni<sub>3</sub>C phase in this data.

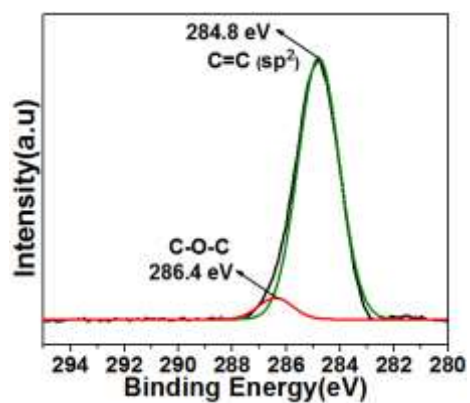
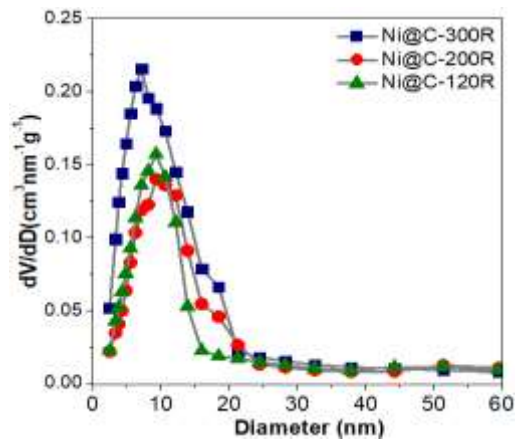
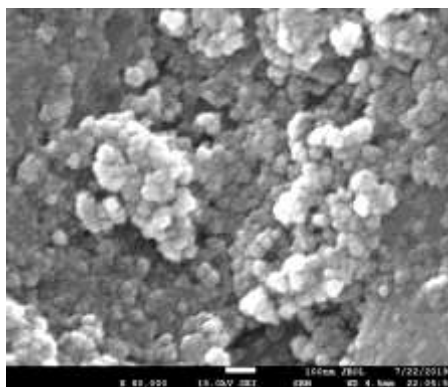


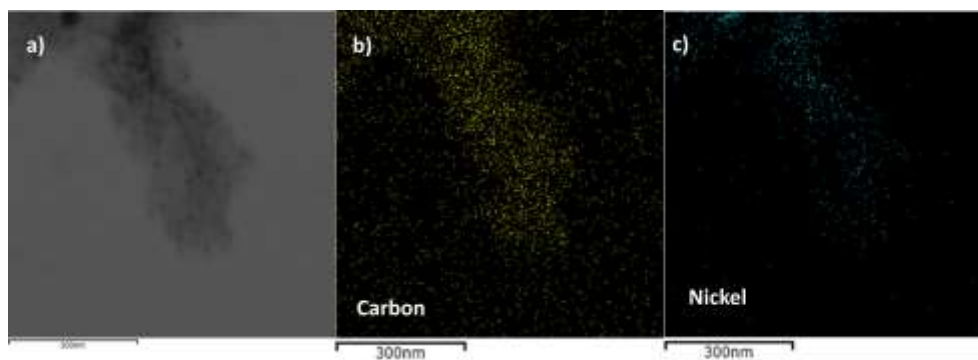
Figure S4: X-ray photoelectron spectrum of carbon present in Ni@C-300R material.



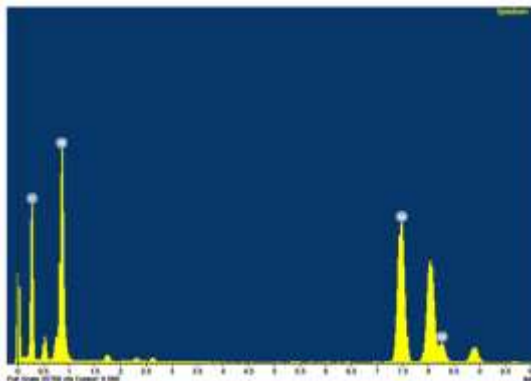
**Figure S5:** The BJH (Barrett, Joyner, and Helendap) pore size analysis of Ni@C-120R, Ni@C-200R, and Ni@C-300R materials.



**Figure S6:** Characterization of Ni@C-300R material: scanning electron microscopy (SEM) image of Ni@C-300R material.



**Figure S7:** Elemental mapping of Ni@C-300R using energy dispersive X-ray analysis (EDXA) a) bright-field image, b) carbon in yellow color, and c) nickel in blue color.



**Figure S8:** Energy Dispersive X-Ray analysis (EDX) of Ni@C-300R material catalysis.

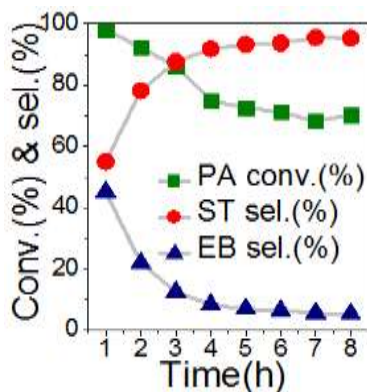
**Table S1:** Quantitative elemental analysis of EDX data for Ni@C-300R material.

S.No.	Element	Weight %
1	Nickel	44.09
2	Carbon	55.91

## 4. Catalysis

### 4.1. Hydrogenation of phenylacetylene (PA) over Ni@C-120R at different temperatures

Styrene synthesis from phenylacetylene was carried out in a fixed-bed continuous down-flow quartz reactor. After the synthesis of Ni@C-120R material in the quartz reactor as described in section-S2.1, the semi-hydrogenation of PA was carried out by passing PA and H<sub>2</sub> gas over the catalyst bed. PA (0.1259mmol/min) was fed into the pre-heater (maintained at 150 °C and placed at the starting of the reactor) using a syringe pump and at the same time, H<sub>2</sub> gas (0.8928 mmol/min) was also introduced into the pre-heater. The feed after passing through the catalyst bed was condensed into a liquid using the ice-trap (maintained at ~4 °C). Samples were collected at the time interval of one hour. The products were identified by gas chromatography (GC, Agilent-7820A, and column: HP-5, 30 m × 0.32 mm × 0.25 μm). The temperature of the catalyst bed was maintained at 60 °C, 70 °C, 80 °C or 90 °C.



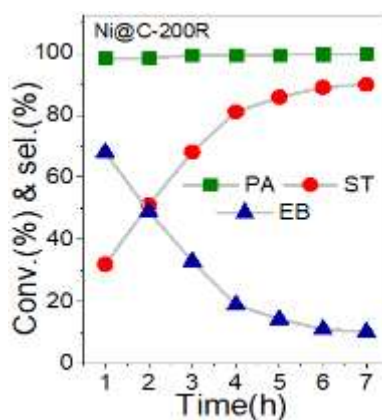
**Figure S9:** Plot of conversion and selectivity versus time (h) in the hydrogenation of phenylacetylene at a) 90 °C over Ni@C-120R material.

**Table S2:** Reaction parameters.

S. No	Temp. (°C)	H <sub>2</sub> flow rate (mmol. /min)	Feed rate (mmol./min)	Mole ratio (H <sub>2</sub> to PA)	PA Conv. (%) <sup>[a]</sup>	ST sent. (%) <sup>[b]</sup>
1	60	0.892	0.125	7.0: 1	7.0	87.7
2	70	0.892	0.125	7.0: 1	12.8	87.3
3	80	0.892	0.125	7.0: 1	30.0	92.3
4	90	0.892	0.125	7.0: 1	70.1	93.7

<sup>[a]</sup> and <sup>[b]</sup> conversion and selectivity have been taken at 7 h for all cases.

#### 4.2. Semi-hydrogenation of phenylacetylene over Ni@C-200R catalyst

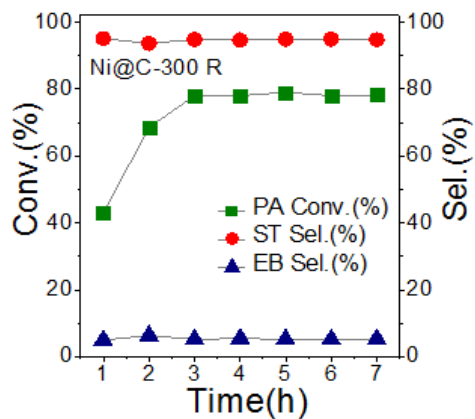


**Figure S10:** Time-on-stream study for the first regeneration of Ni@C-200R catalyst. Reaction conditions: 7:1 molar ratio between H<sub>2</sub> and PA and the reaction carried at 90 °C.

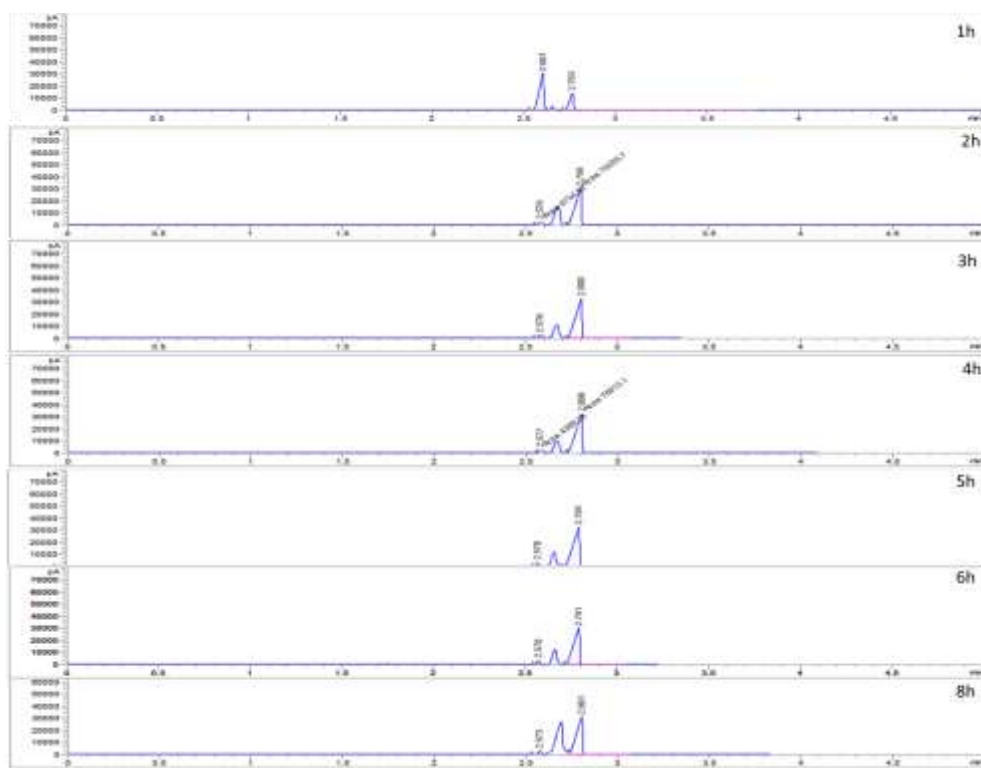
#### 4.2. Semi-hydrogenation of phenylacetylene (PA) over Ni@C-300R catalyst

### 4.2.1 Effect of WHSV

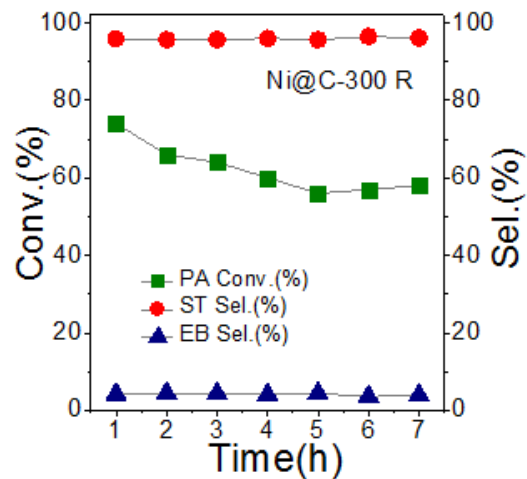
The reactions were carried out as described in section 4.1 at 90 °C. Different amounts of PA have been fed into the reactor to achieve different WHSV values as outlined in Table S3.



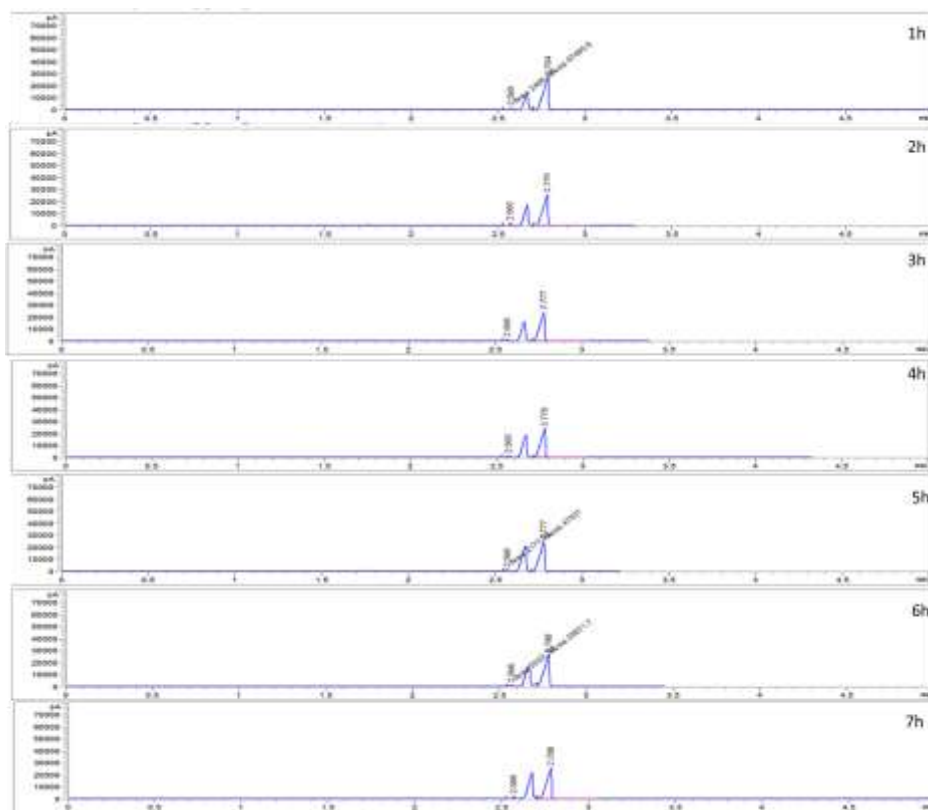
**Figure S11:** Time-on-stream study: conversions of PA over Ni@C-300R. *Reaction conditions:* 0.1 g of catalyst, WHSV: 3.78 h<sup>-1</sup> and 90 °C.



**Figure S12:** Gas chromatograms: The retention time of ethylbenzene, phenylacetylene, and styrene are 2.57 min, 2.68 min, and 2.78, respectively. *Reaction conditions:* 0.1 g of catalyst, WHSV: 3.78 h<sup>-1</sup> and 90 °C.

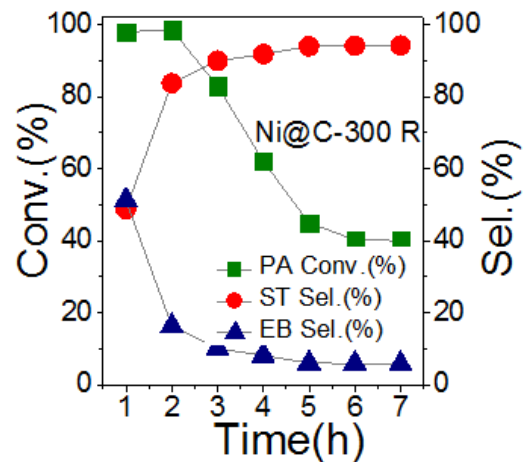


**Figure S13:** Time-on-stream study: conversions of PA over Ni@C-300R. Reaction conditions: 0.1 g of catalyst, WHSV:  $11.34 \text{ h}^{-1}$  and  $90^\circ\text{C}$ .

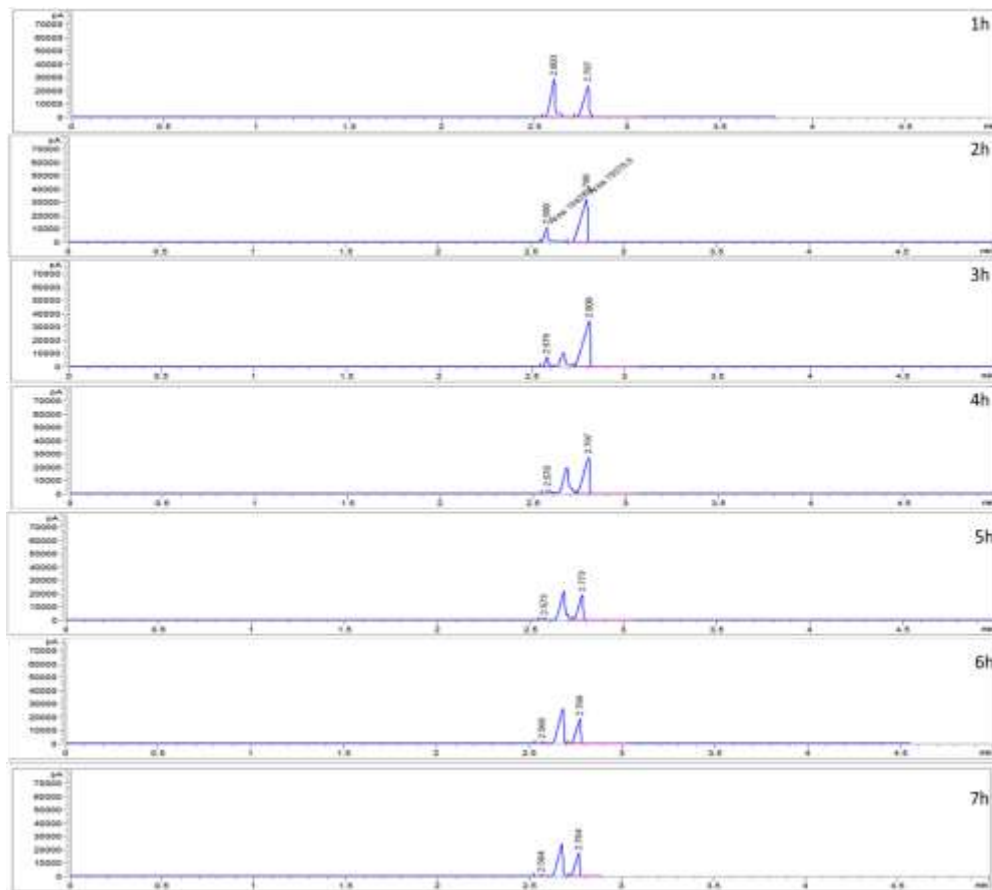


**Figure S14:** Gas chromatograms: The retention time of ethylbenzene, phenylacetylene, and styrene are 2.57 min, 2.68 min, and 2.78, respectively. Reaction conditions: 0.1 g of catalyst, WHSV:  $11.3 \text{ h}^{-1}$  and  $90^\circ\text{C}$ .





**Figure S15:** Time-on-stream study: conversions of PA over Ni@C-300R. Reaction conditions: 0.1 g of catalyst, WHSV: 15.2 h<sup>-1</sup> and 90 °C.



**Figure S16:** Gas chromatograms: The retention time of ethylbenzene, phenylacetylene, and styrene are 2.57 min, 2.68 min, and 2.78, respectively. Reaction conditions: 0.1 g of catalyst, WHSV: 15.2 h<sup>-1</sup> and 90 °C.

**Table S3:** Reaction parameters for the optimization of WHSV

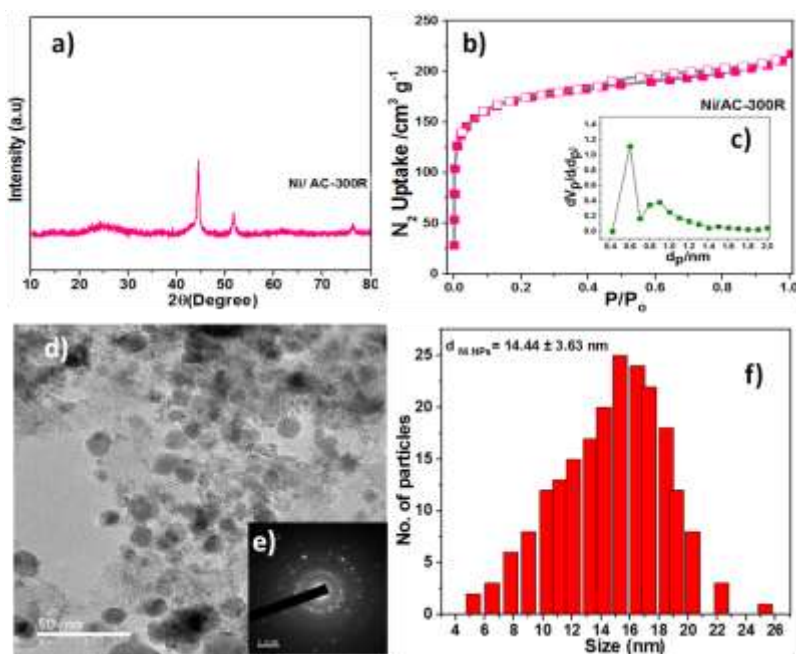
S. No	Feed amount (mmol. /h)	PA Conv. (%) <sup>[a]</sup>	ST sent. (%) <sup>[b]</sup>	WHSV <sup>[c]</sup> (h <sup>-1</sup> )
1	4.5	78.0	94.8	3.78
2	9.1	99.3	91.8	7.56
3	13.6	57.0	96.4	11.34
4	18.2	40.2	94.1	15.12

<sup>[a]</sup> and <sup>[b]</sup> conversion and selectivity have been taken at 7 h for all cases. <sup>[c]</sup> WHSV: Hourly mass feed flow rate/ catalyst weight.

### 4.3. Hydrogenation of phenylacetylene over Ni/AC-300 material

#### 4.3.1. Synthesis of Ni/AC-300 material

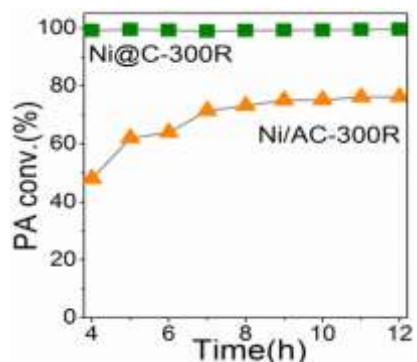
Ni/AC-300 was prepared through the impregnation method.<sup>2</sup> 1.0 g of activated carbon (AC) and 1.783 g of Ni (NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were mixed in 200 mL of water and stirred for two hours. After completion of reaction time, the reaction mixture was dried at 100 °C overnight. The material was loaded into the flow reactor and pretreated at 300 °C for 3h under N<sub>2</sub> flow. The material was reduced at the same temperature for 2 h under H<sub>2</sub> flow (20 mL/min) in the next step.



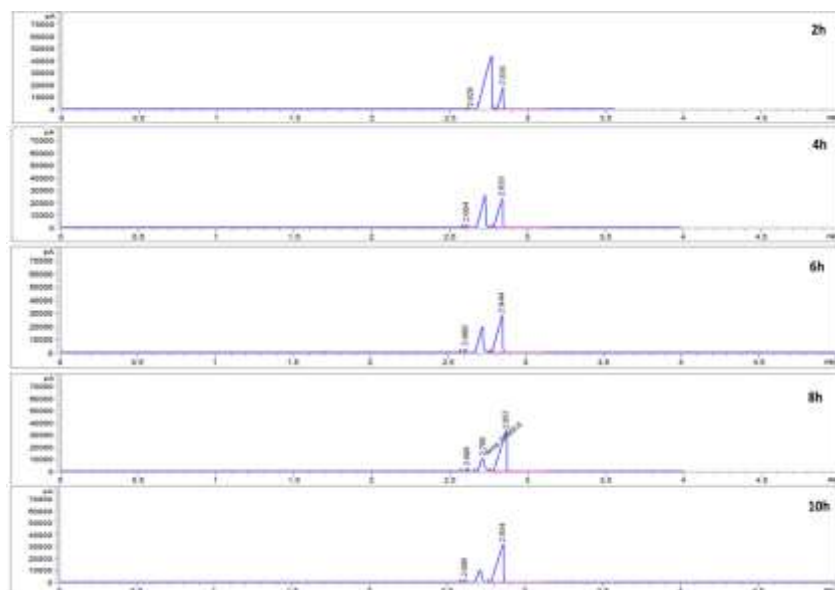
**Figure S17:** Characterization of Ni/AC-300R material: a) Powder X-ray diffraction pattern, b) N<sub>2</sub> isotherm at 77K) MP plot, d) bright field-TEM image e) Selective electron diffraction (SAED) pattern and f) size distribution histogram of Ni/AC-300R.

### 4.3.2. Time on-stream study over Ni/AC-300R material

In a typical catalysis study, fresh catalyst Ni/AC was loaded into a quartz reactor and then treated at 300 °C according to section 2.1, and the catalyst was reduced under H<sub>2</sub> flow at 300 °C for 2 h. PA's typical hydrogenation was carried at 90 °C over fresh Ni/AC-300R material under a 1:7 mole ratio of PA to H<sub>2</sub>.



**Figure S18:** Comparison of time-on-stream study between Ni@C-300R and Ni/AC-300R. A plot of PA conversion versus time (h). *Reaction conditions:* 0.1 g of catalyst, 20 mL of H<sub>2</sub>/min, WHSV: 7.56 h<sup>-1</sup> and 90 °C.



**Figure S19:** Gas chromatograms of time-on-stream study over Ni/AC-300R material. The retention times of ethylbenzene, phenylacetylene, styrene are 2.6 min, 2.7 min, and 2.8, respectively. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA, and the reaction was carried at 90 °C.

#### 4.4. Density functional theory (DFT) method

The structure and activity of PA, ST, and EB on Ni<sub>3</sub>C and Ni@C surface was studied by density functional theoretical (DFT) methods. The structure model for the calculations was generated based on the experimental crystal structures. These models were optimized using the Kohn-Sham self-consistent DFT method as implemented in the SIESTA (Spanish Initiative for Electronic Simulations with Thousands of Atoms) package,<sup>3</sup> which consists of localized molecular-orbital basis sets. The exchange-correlation functional, E<sub>xc</sub> using generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE)<sup>4</sup> and Troullier Martins norm-conserving nonlocal pseudopotentials in the Kleinman Bylander form was used to describe atomic core in all calculations in order to improve the computational efficiency. A double-zeta basis (DZP) set with the polarization orbital was used for all atoms and a pseudo atomic orbital basis set was used for Ni with a real-space mesh cut-off of 300 Ry. The close-packed Ni(110), Ni<sub>3</sub>C(010) surface was exposed by a 2 × 1 unitcell with three layers in the slab model. The layers were allowed to relax during optimization. The sampling of the Brillouin zone was done with 6 × 6 × 1 k-point grids. A vacuum region of 10 Å is placed over the slab to avoid interactions with neighboring unitcell. All models were relaxed until the interatomic force was 0.01 eV Å<sup>-1</sup>. The atomic coordinates were relaxed with convergence criteria of 0.05 eV for energy and 0.05 Å for displacement. For Ni@C surface a close-packed Ni<sub>3</sub>C(010) surface with three layers in the slab model was generated; a top nickel layer and bottom two carbon layers. The layers were relaxed as described above. Bands were calculated at the same k-point grid to check the contributions of atomic orbitals to the bands near the Fermi level at the  $\Gamma$ -point. Note that surface states only have contribution coming from atoms close to the surface of the slab. For calculation of the PA, ST, and EB binding energies, a molecule of PA, ST, and EB was placed on top of the surface and the top layer was allowed to interact with the adsorbate while the bottom layers were constrained. The adsorbate molecule was located above the surface at distances that were chosen to be within the range of physical interactions but longer than the corresponding chemical bond distances. The adsorption energies  $\Delta E_{ads}$  were calculated by,

$$\Delta E_{ads} = E_{adsorbate/Ni_3C/Ni@C} - [E_{adsorbate} + E_{slab}]$$

where  $\Delta E_{ads}$  is the adsorption energy,  $E_{adsorbate/Ni_3C/Ni@C}$  is the energy of Ni<sub>3</sub>C or Ni@C slab with PA, ST, and EB molecules adsorbed on surface,  $E_{adsorbate}$  is the energy of adsorbate in gas phase, and  $E_{slab}$  is the energy of Ni<sub>3</sub>C and Ni@C slab. Force constants were evaluated in each case to confirm the energy minimum and transition states (Single imaginary frequency).

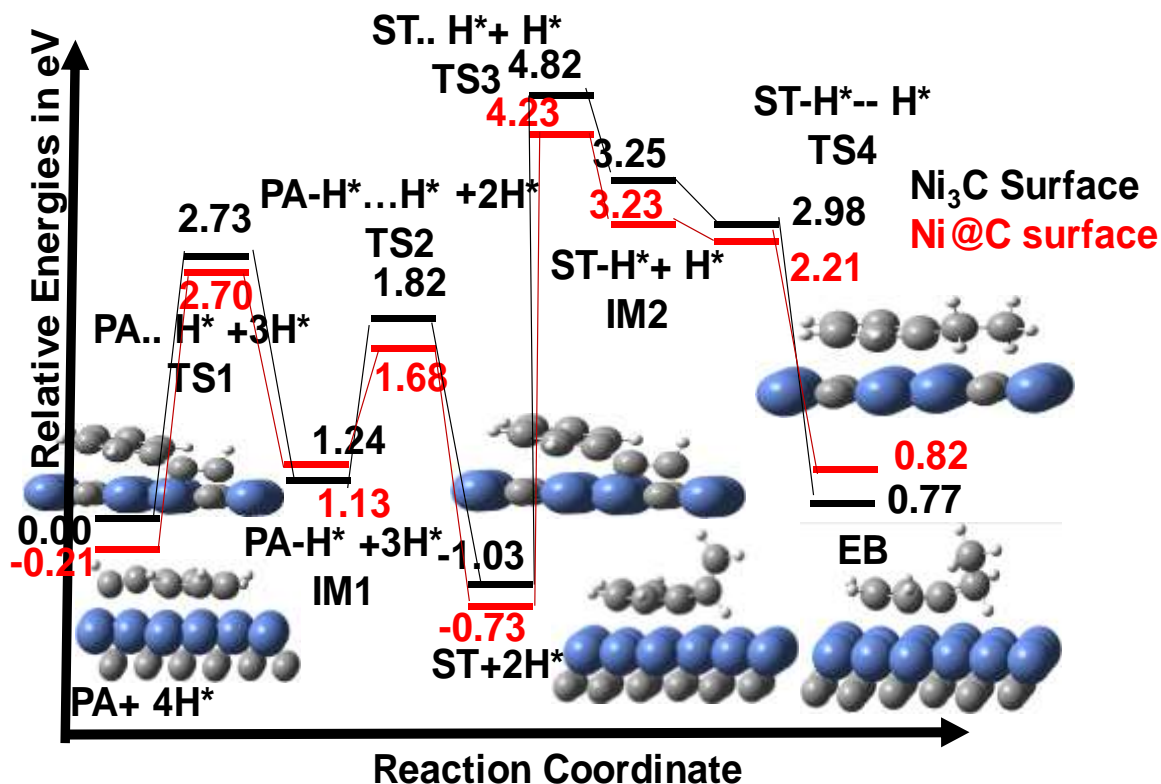


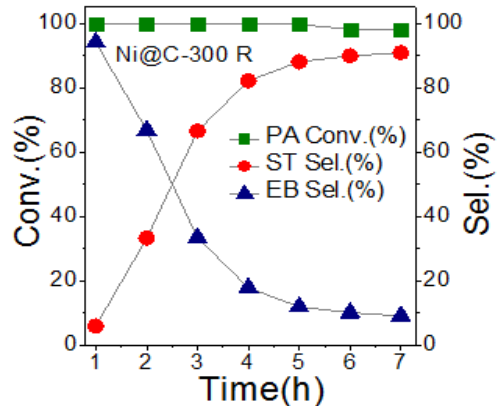
Figure S20: Relative energy profile for the conversion of PA to EB in Ni<sub>3</sub>C/Ni@C surface through transition states/intermediates TS1, IM1, TS2, ST, TS3, IM2 and TS4.

#### 4.5. Selective semi-hydrogenation of PA in the presence of an excess of ST

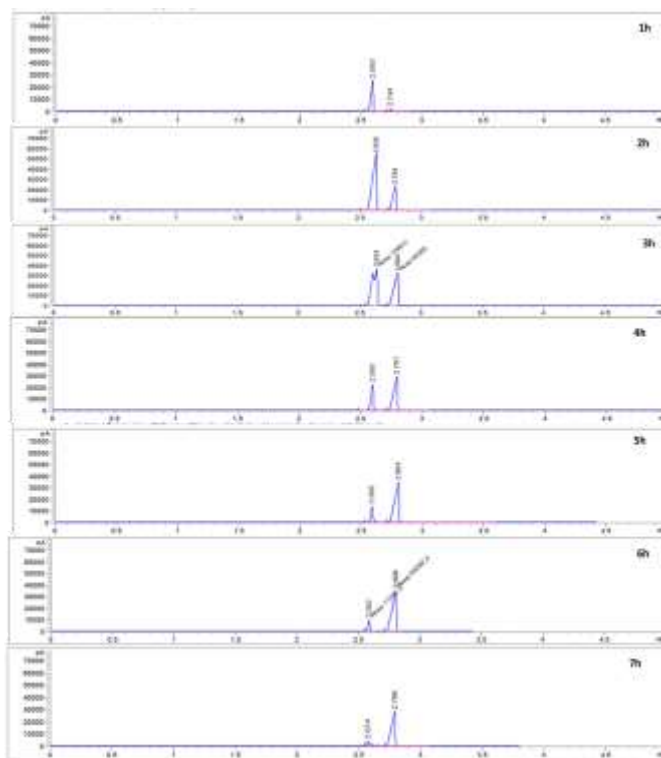
The reaction was carried out as described in section 4.1 at 90 °C. The mixture of ST (98.2 %) and PA (1.8 %) was fed into the reactor. The H<sub>2</sub> flow rate was maintained constant at 20 mL/min. The reaction was carried out for 7h. And for every one hour, the product was analyzed using GC chromatography.

#### 4.6. Regeneration of Ni@C-300R catalyst

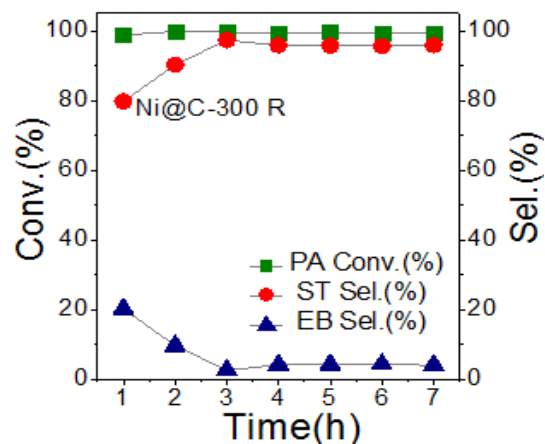
After completion of the reaction, the catalyst bed temperature was increased to 300 °C under N<sub>2</sub> (20 mL/min) flow. After reaching 300 °C, the catalyst was treated with H<sub>2</sub> flow (20 mL/min) for 2h. Finally, the bed temperature was brought to 90 °C and carried the reaction for the next cycle. The same procedure was used for all regeneration cycles of Ni@C-300R catalyst.



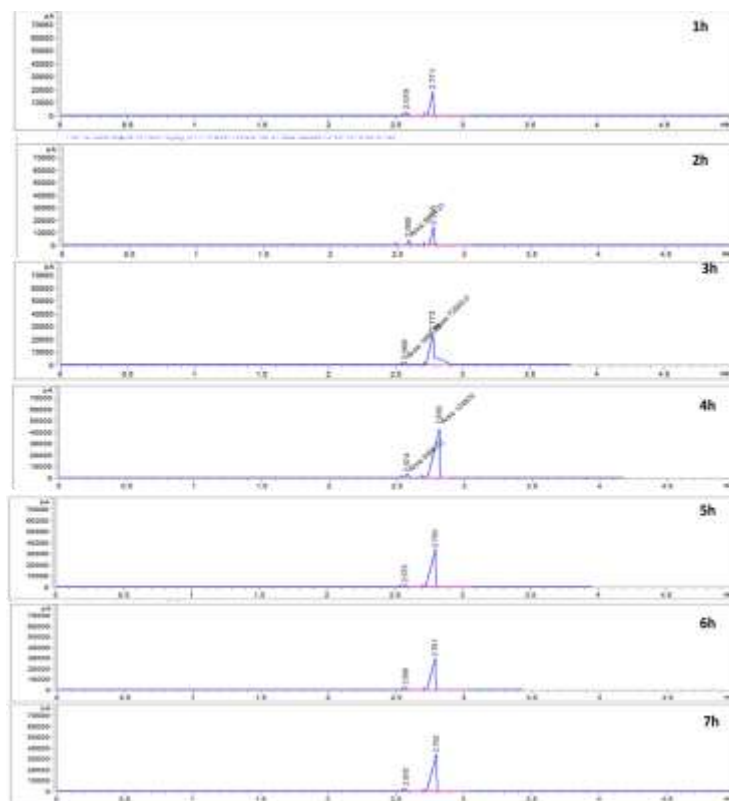
**Figure S21:** Time-on-stream study for the first regeneration of Ni@C-300R catalyst. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA and the reaction carried at 90 °C



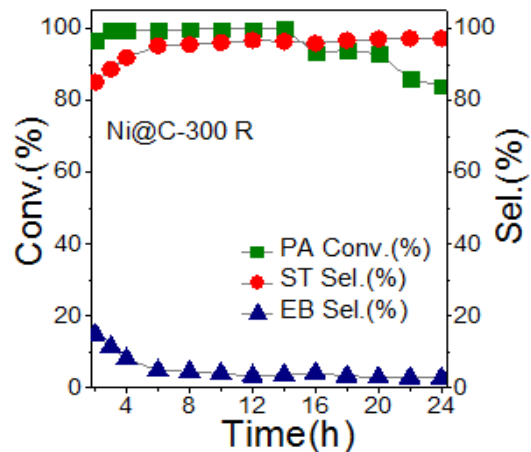
**Figure S22:** Gas chromatograms for first regeneration (1st) product analysis over Ni@C-300R material. The retention time of ethylbenzene, phenylacetylene, and styrene are 2.57 min, 2.68 min, and 2.78, respectively. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA, and the reaction carried at 90 °C.



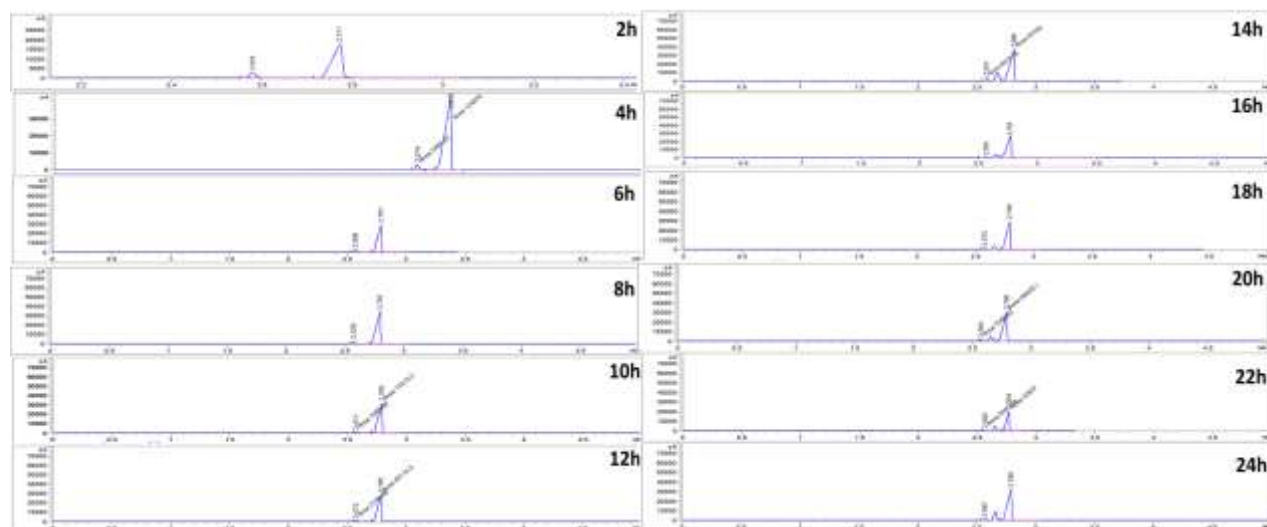
**Figure S23:** Time-on-stream study for second regeneration of Ni@C-300R catalyst. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA and the reaction carried at 90 °C.



**Figure S24:** Gas chromatograms for second regeneration (2nd) product analysis over Ni@C-300R material. The retention time of ethylbenzene, phenylacetylene, and styrene are 2.57 min, 2.68 min, and 2.78, respectively. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA, and the reaction carried at 90 °C.



**Figure S25:** Time-on-stream study for third regeneration of Ni@C-300R catalyst. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA and the reaction carried at 90 ° C K.



**Figure S26:** Gas chromatograms for third regeneration (3<sup>rd</sup>) product analysis over Ni@C-300R material. The retention time of ethylbenzene, phenylacetylene, and styrene are 2.57 min, 2.68 min, and 2.78, respectively. *Reaction conditions:* 7:1 molar ratio between H<sub>2</sub> and PA, and the reaction carried at 90 ° C.



## 5. Characterization of spent catalyst

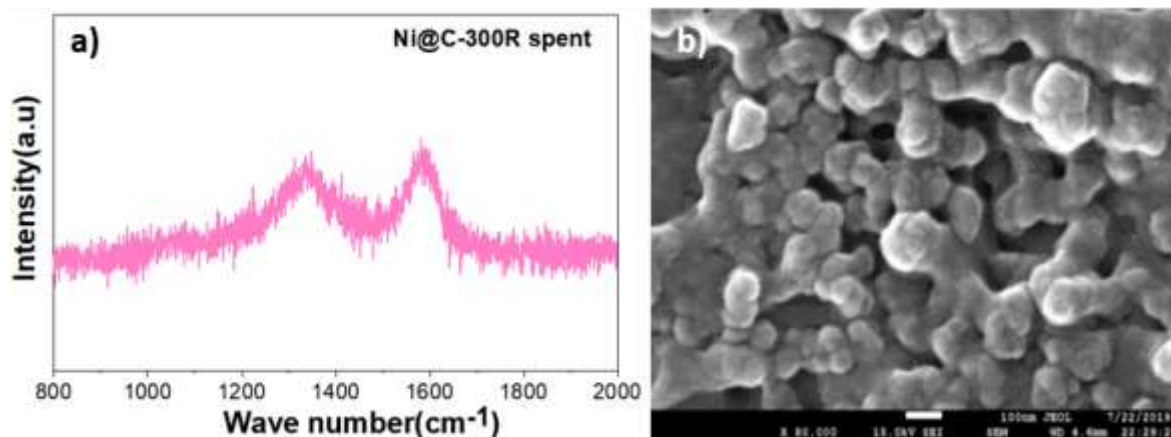


Figure S27: Characterization of spent catalyst: a) Raman spectra, and b) SEM of Ni@C-300R material.

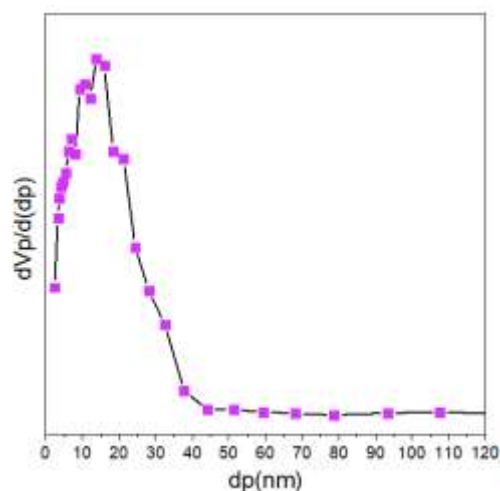


Figure S28 : BJH pore size analysis of Ni@C-300 R catalyst after four cycles.

## 6. Semi-hydrogenation of alkynes in a batch reactor

We carried out semi-hydrogenation of three more substrates in a batch reactor (Fischer bottle) material under 1 bar H<sub>2</sub> at 90 °C for 4h. Before the reaction, the reactor was charged with 2.57 mg (10 wt %) of the catalyst to the substrate (25.57 mg, 0.25 mmol) in a 1 mL of ethanol solvent, and the reactor was closed. To avoid moisture from the reactor, the reactor was purged with H<sub>2</sub> gas three times and finally kept under 1bar H<sub>2</sub>. The reaction was carried out at 90 °C under 1 bar H<sub>2</sub> for 4 h.

## 6.1. Literature about vapor phase and batch hydrogenation process over nickel-based catalysts

**Table S4:** Literature of phenylacetylene hydrogenation over Ni-based materials under a fixed bed downflow reactor.

S. No	Catalyst	Temp. (°C)	PA Conv. (%)	Selectivity (%)		Ref
				ST	EB	
1	Ni@C	150	90	60	40	<i>Russian Journal of Physical Chemistry A</i> , 2014, 88, 12-16.
2	Ni ND	150	80	55	45	<i>Journal of Catalysis</i> , 2016, 344, 90–99.
3	Ni/Al <sub>2</sub> O <sub>3</sub>	100	40	84	16	<i>Russian Journal of Physical Chemistry A</i> , 2012, 86, 1800-1807.
4	Ni/Al <sub>2</sub> O <sub>3</sub>	150	48	75	25	
5	Ni/Al <sub>2</sub> O <sub>3</sub>	200	85	40	60	
6	Ni@C	150	90	60	40	<i>Carbon</i> , 2014, 74, 291-301.

**Table S5:** Literature of phenylacetylene hydrogenation over Ni-based materials through the batch process.

S. No	Catalyst	Reaction conditions			PA Conv. (%)	Selectivity (%)		Ref
		Temp. (°C)	Press. (H <sub>2</sub> ) bar	Time (h)		ST	EB	
1	Ni NSs	50	1.0	20	98.0	89.0	11.0	<i>Nanoscale</i> , 2018,10, 6936-6944
2	SGR/PANI/Ni	27	6.8	24	-	82	-	<i>Ind. Eng. Chem. Res.</i> 2015, 54, 11493–11499
3	SGR/Ni	27	6.8	24	-	52	-	-
4	PANI/Ni	27	6.8	24	-	64	-	-
5	Ni	50	3.5	4	60	35	65	<i>Catal. Sci. Technol.</i> , 2016,6, 708-712
6	Ni <sub>2</sub> Si/SiO <sub>2</sub>	40	10.0	4	79.0	87.7	12.3	<i>Catal. Today</i> , 2015, 246, 176–183.
7	NiSix	50	4.1	3	>99.9	90	10	<i>Ind. Eng. Chem. Res.</i> 2012, 51, 3604–3611
8	Ni <sub>2</sub> P/Al <sub>2</sub> O <sub>3</sub>	100	3.0	3	>99.5	88.5	11.5	<i>ACS Catal.</i> 2015, 5, 5756-5765.
9	Ni <sub>2</sub> P	85	6.0	6	98	96.		10.1016/j.nantod.2011.12.003
10	Ni-fructose@SiO <sub>2</sub> -800	80	10.0	5	>99.9 (DPA)	97.0 (E/Z)	3.0	<i>Journal of Catalysis</i> 370 (2019) 372–377.
11	Ni NPS/[CNC <sub>3</sub> MMIM] NTF <sub>2</sub>	50	4.0	17	100	79	21	<i>Chem. Commun.</i> 2016, 52, 9129–9132.
12	Ferrite–Ni	27	6.8	48	>99.9	80	20	<i>Green Chem.</i> , 2009, 11, 127–131

## 7. References

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