Supplementary Information (SI) for Materials Advances.

Supporting Information

Carbon Supported Nickel Sulphide Catalyts for Transfer Hydrogenation of Nitroarenes to Aryl amines

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1. Literature comparison

Table S1. Comparison of our catalyst with other reported catalysts for the hydrogenation of nitroarenes.

entry	catalyst	H_2 source	T (°C)	t (h)	yield (%)	reference
1	Ni_3S_2/C	$N_2H_4 \cdot H_2O$ (10 mmol)	70	6	91	This work
2	Co1/NPC	H_2 (30 bar)	110	1.5	>99	1
3	Co/MA-800	H_2 (40 bar)	120	18	96	2
4	Co/NC	H_2 (30 bar)	110	8	97.4	3
5	Co@C/CNT	$N_2H_4 \cdot H_2O$ (2 mmol)	25	9	99	4
6	Co-L@C-800	$N_2H_4 \cdot H_2O$ (0.48 mmol)	50	6	99	5
7	Co@C-800-AL	Methanol	140	24	95	6
8	Co@NC/AC	H_2 (10 bar)	110	4	99	7
9	Co@NCT	$N_2H_4 \cdot H_2O$ (1 mL)	40	0.34	99	8
10	Co@NC-600	Formic acid	90	4	99.9	9
11	Ni_2P-AC	$N_2H_4 \cdot H_2O$ (0.5 mL)	70	2	93	10
12	Ni-N-C-700	H_2 (30 bar)	120	8	99	11
13	Ni/C_{60}	H_2 (20 bar)	90	0.66	99	12
14	Ni/SiO_2	$N_2H_4 \cdot H_2O$ (2 mmol)	100	8	93.8	13
15	Fe-Fe_3C-Fe_3O_4@CN	$N_2H_4 \cdot H_2O$ (1.6mmol)	85	9	95.2	14
16	γ-Fe_2O_3/LRC-700	H_2 (35 bar)	120	18	96	15
17	Nano 2H-WS_2	H_2 (50 bar)	120	8	98	16
18	NiCu/C@SiO_2-800	H_2 (20 bar)	120	0.6	>99	17
19	ImmFe-IL	$N_2H_4 \cdot H_2O$ (3 mmol)	110	12	99	18
20	FeS_2	$N_2H_4 \cdot H_2O$ (20 mmol)	60	-	99	19
21	Fe@C	H_2 (11.5 bar)	100	0.67	99	20
22	Cu/celite	Ethylene glycol	100	1	97	21
23	MoOx/ZSM-5	H_2 (50 bar)	120	20	99	22
24	Ru/PNC-700	H_2 (10bar)	80	24	95	23
25	Ru/OMC-800	H_2 (40 bar)	50	2	99	24
26	Ru/MoS_2	H_2 (30 bar)	100	2.5	94	25
27	Ir-MoOx/SiO_2	H_2 (10 bar)	50	0.5	99	26
28	ZrO_2@Pt	H_2 (10 bar)	25	1	99	27
29	Pt/CeO_2	H_2 (10 bar)	25	2	87	28
30	Rh/COF	H_2 (1 bar)	25	19	99	29
31	$NiPd/TiO_2$	H_2 (10 bar)	80	0.5	99	30

<table>
<tr><td>32</td><td>AuPd/TiO_2</td><td>H_2 (3 bar)</td><td>90</td><td>15</td><td>99</td><td>31</td></tr>
<tr><td colspan="7">NPC (nitrogen- and phosphorous-doped carbon); MA-800 (macroalgae-derived carbon, carbonized at 800 °C); NC (nitrogen-doped carbon); CNT (carbon nanotube); L@C-800 (ligand-derived carbon, carbonized at 800 °C); AC (activated carbon); LRC-700 (lignin-derived carbon, carbonized at 700 °C); C@SiO_2-800 (*In-situ* carbon supported silica, carbonised at 800 °C); IL (Ionic liquid); PNC-700 (phosphorous- and nitrogen-doped carbon); OMC-800 (ordered mesoporous carbon, carbonized at 800 °C); COF (Covalent organic framework)</td></tr>
</table>

2. Catalyst characterization

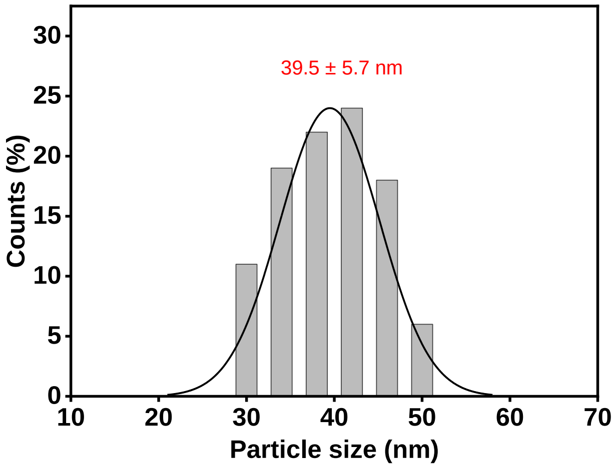


Fig. S1. Particle size distribution of Ni_3S_2/C, determined by TEM imaging.

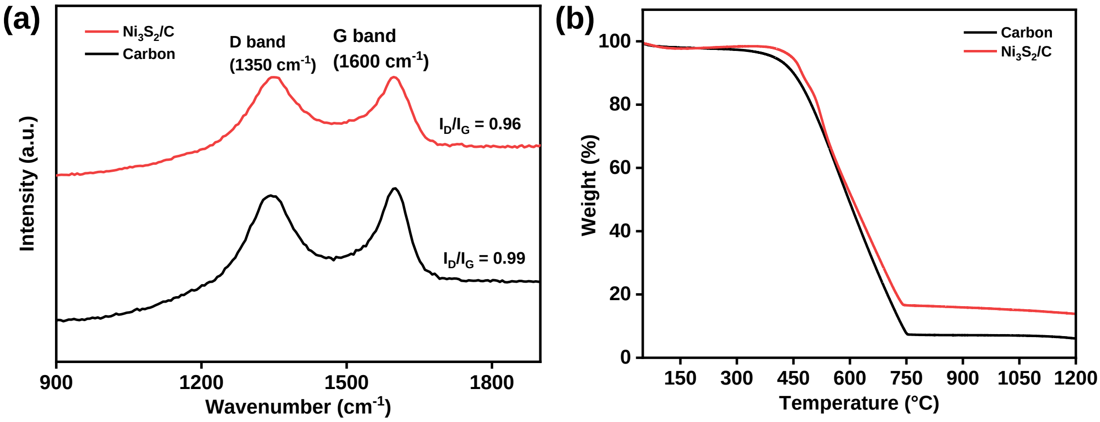


Fig. S2. (a) Raman spectra and (b) thermogravimetric analysis of carbon as support material and the Ni_3S_2/C catalyst. The Ni_3S_2/C catalyst exhibits a higher residual mass than the pristine carbon support, confirming the successful incorporation of thermally stable Ni_3S_2 species over the carbon support.

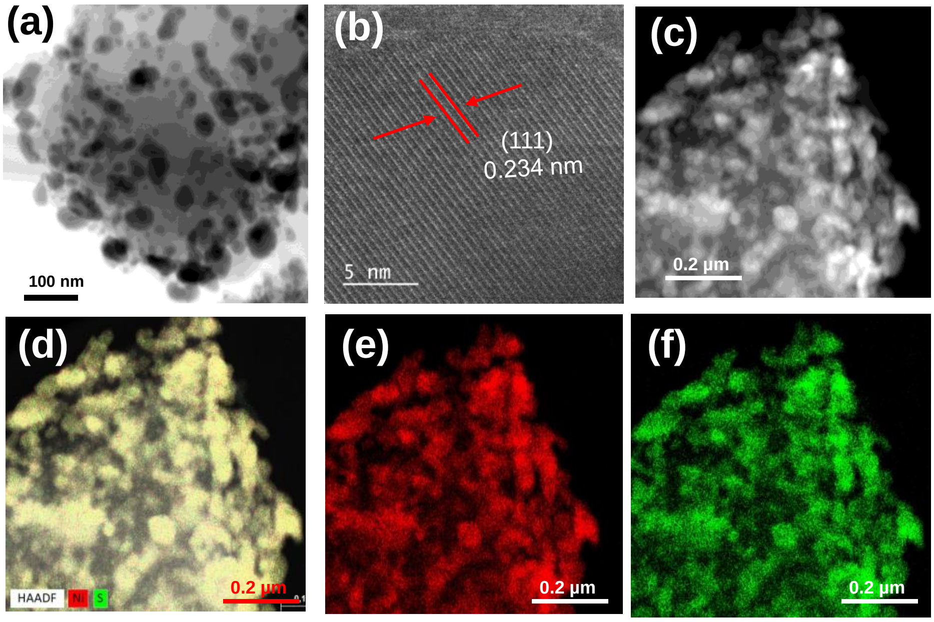


Fig. S3. (a) TEM overview image of the spent Ni_3S_2/C catalyst, (b) HRTEM image of a single nanoparticle, showing lattice fringes, (c) HAADF-STEM image with (d-f) EDX mapping of nanoparticles on HAADF-STEM image in (c) with element maps of (d) combined Ni and S, (e) Ni (red), and (f) S (green).

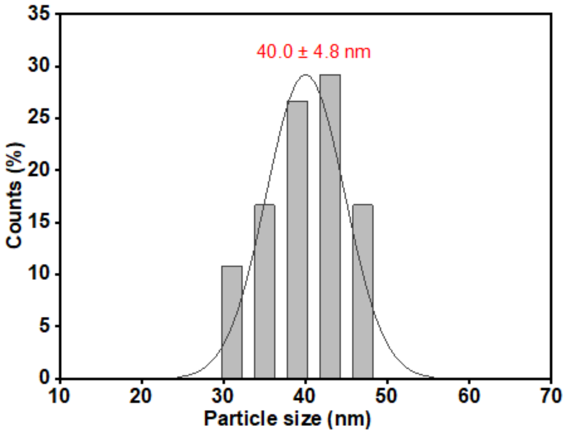


Fig. S4. Particle size distribution plot of the spent Ni_3S_2/C catalyst, determined by TEM imaging.

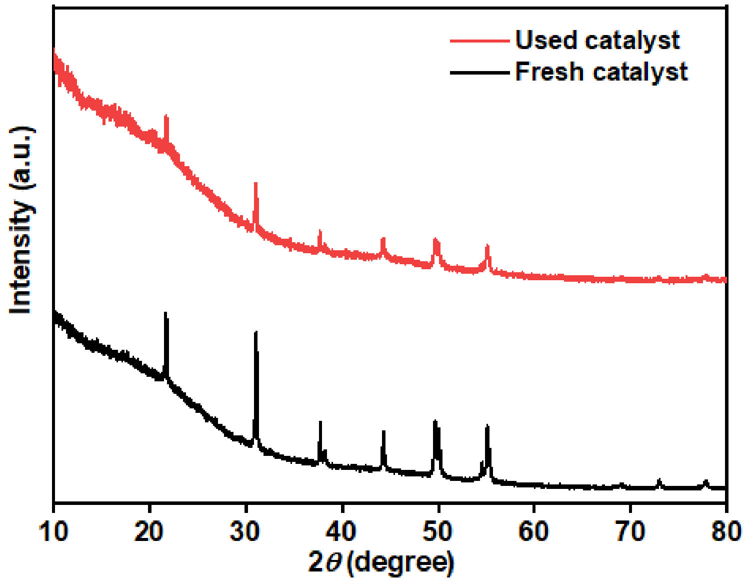


Fig. S5. Powder X-ray diffractogram of the spent and fresh Ni_3S_2/C catalyst.

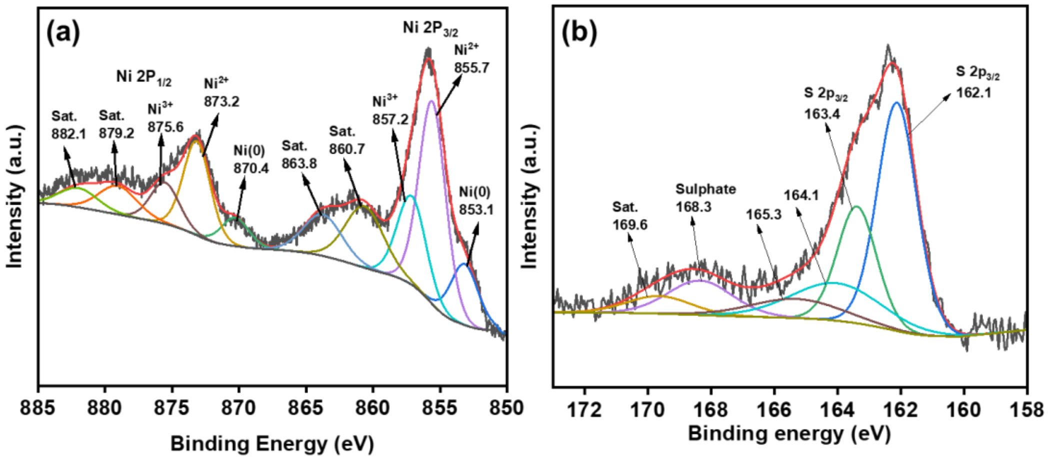


Fig. S6. XPS spectra (a) Ni 2p and (b) S 2p region of spent Ni_3S_2/C catalyst.

3. GC-MS analysis

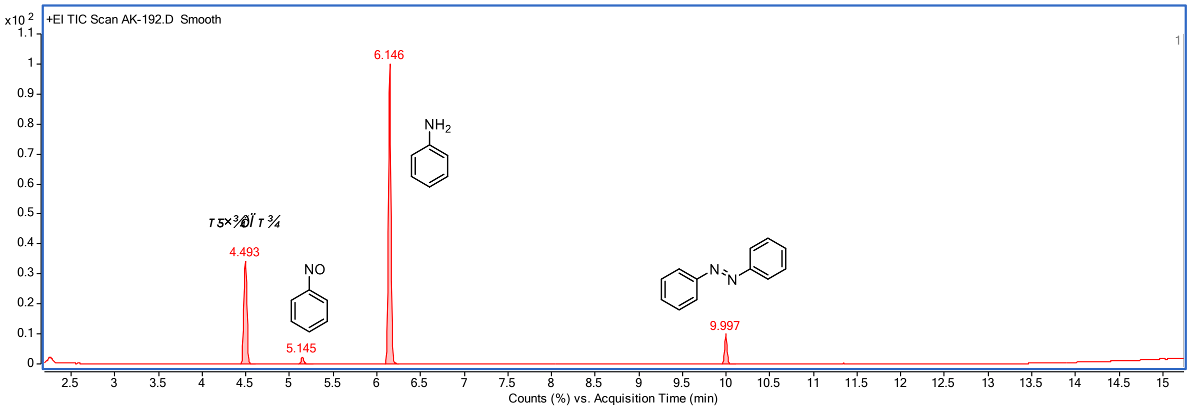


Fig. S7. Catalytic transfer hydrogenation of nitrobenzene to aniline over Ni_3S_2/C. Reaction conditions: nitrobenzene (1 mmol), Ni_3S_2/C (30 mg, 10 wt%), *n*-heptane (2 mL), 70 °C, hydrazine monohydrate (10 equiv.), 6 h.

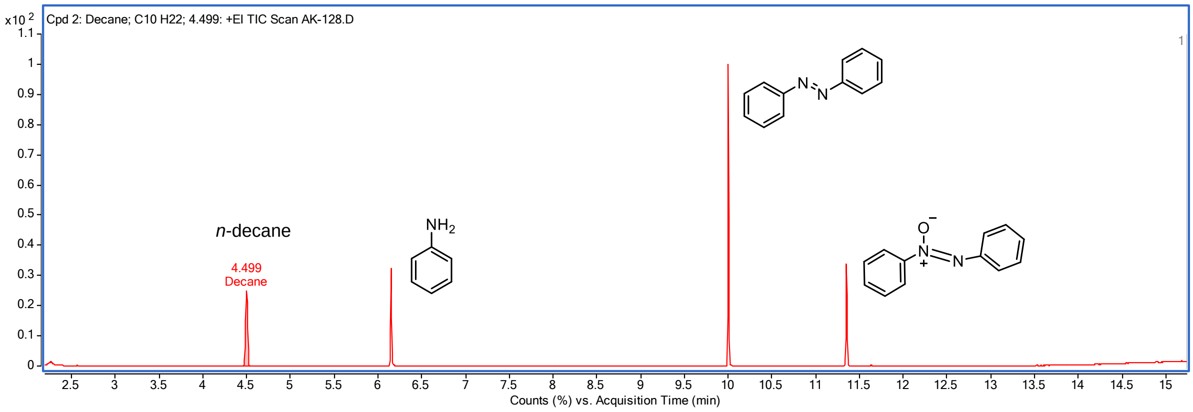
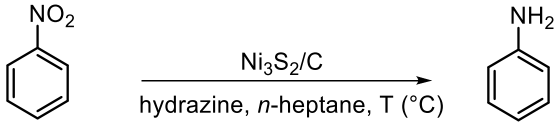


Fig. S8. Catalytic transfer hydrogenation of nitrobenzene to aniline over Ni/C. Reaction conditions: nitrobenzene (1 mmol), Ni/C (30 mg, 10 wt%), *n*-heptane (2 mL), 70 °C, hydrazine monohydrate (10 equiv.), 2 h.

4. Catalytic test results

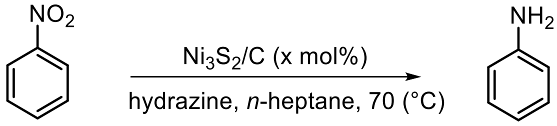
Table S2. Effect of the temperature in the transfer hydrogenation of nitrobenzene.[a]



entry	**T (°C)**	**t (h)**	**Conv. (%)**	**Aniline yield (%)**
1	30	2	-	-
2	40	2	21	11
3	50	2	40	12
4	60	2	60	40
5	70	2	>99	64

[a] Reaction conditions: nitrobenzene (0.97 mmol, 0.1 mL), catalyst (30 mg, 10 wt% Ni), *n*-heptane (2 mL), 30-70 °C, hydrazine monohydrate (10 equiv.). Conversion, selectivity and yield were calculated by GC-MS with *n*-decane as external standard.

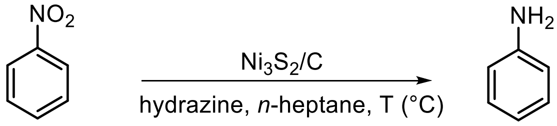
Table S3. Effect of the catalyst loading in the transfer hydrogenation of nitrobenzene.[a]



entry	**Catalyst loading (mol%)**	**t (h)**	**Conv. (%)**	**Aniline yield (%)**
1	0.87	2	65	35
2	1.73	2	85	33
3	3.47	2	>99	45
4	5.2	2	>99	64

[a] Reaction conditions: nitrobenzene (0.97 mmol, 0.1 mL), catalyst (0.87-5.2 mol%), *n*-heptane (2 mL), 70 °C, hydrazine monohydrate (10 equiv.). Conversion, selectivity and yield were calculated by GC-MS with *n*-decane as external standard.

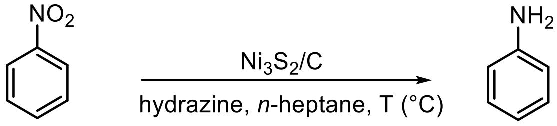
Table S4. Effect of the hydrazine amount in the transfer hydrogenation of nitrobenzene.[a]



entry	Hydrazine (equiv.)	t (h)	Conv. (%)	Aniline yield (%)
1	2	2	40	23
2	4	2	68	28
3	6	2	88	44
4	8	2	94	52
5	10	2	>99	64

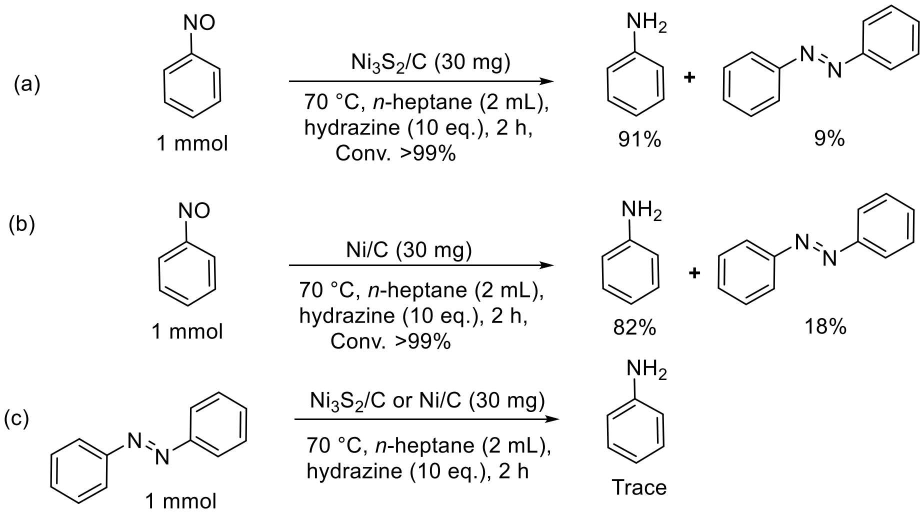
[a]Reaction conditions: nitrobenzene (0.97 mmol, 0.1 mL), catalyst (30 mg, 10 wt% Ni), *n*-heptane (2 mL), 30-70 °C, hydrazine monohydrate (2-10 equiv.). Conversion, selectivity and yield were calculated by GC-MS with *n*-decane as external standard.

Table S5. Effect of the hydrogen source in the transfer hydrogenation of nitrobenzene.[a]

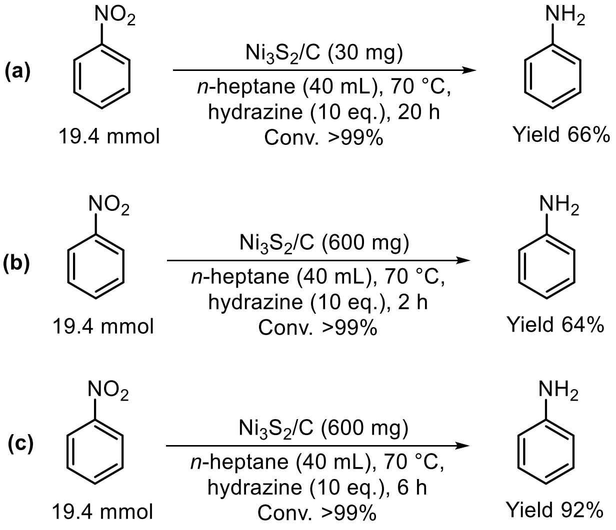


entry	Hydrogen source	t (h)	Conv. (%)	Aniline yield (%)
1	methanol	2	-	-
2	ethanol	2	-	-
3	Formic acid	2	-	-
4	isopropanol	2	-	-
5	hydrazine	2	>99	64

[a]Reaction conditions: nitrobenzene (0.97 mmol, 0.1 mL), catalyst (30 mg, 10 wt% Ni), *n*-heptane (2 mL), 30-70 °C, hydrogen source (10 equiv.). Conversion, selectivity and yield were calculated by GC-MS with *n*-decane asexternal standard.



Scheme S1. Control experiments to investigate the reaction pathway in the catalytic transfer hydrogenation of nitrosobenzene over (a) Ni_3S_2/C, (b) Ni/C and (c) azobenzene over Ni_3S_2/C and Ni/C.



Scheme S2. Gram-scale experiment for the catalytic transfer hydrogenation of nitrobenzene to aniline over Ni_3S_2/C.

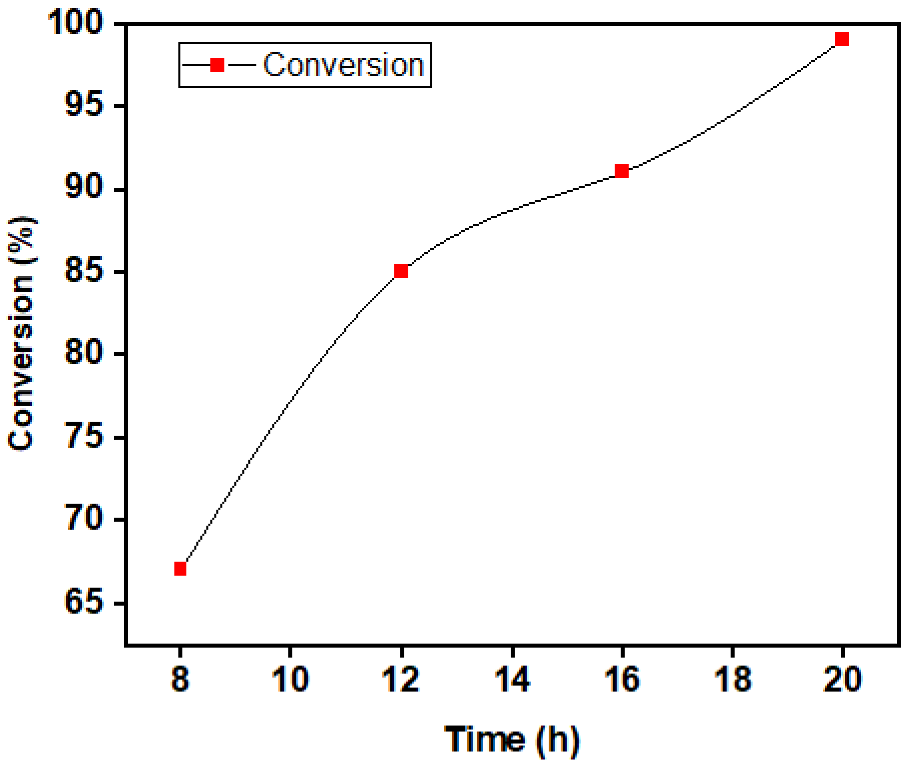


Fig. S9. Time-dependent conversion for the gram-scale reaction. Reaction conditions: nitrobenzene (19.4 mmol), Ni_3S_2/C (30 mg), *n*-heptane (40 mL), hydrazine monohydrate (10 equiv.) and 70 °C.

Table S6. Comparison of the catalytic activity for nitrobenzene transfer hydrogenation.

entry	Catalyst	t (h)	Conv. (%)	Aniline yield (%)
1	Ni_3S_2/C	2	>99	64
2	Ni_2P-AC	2	>99	93

[a]Reaction conditions: nitrobenzene (0.97 mmol, 0.1 mL), catalyst (30 mg), *n*-heptane (2 mL), 70 °C, hydrazine monohydrate (10 equiv.).

5. References

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