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Supplementary Materials for

Heterogeneous Nickel-Catalysed Reversible, Acceptorless Dehydrogenation of N-Heterocycles for Hydrogen Storage

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S1. Materials and methods

All reactions were performed in oven (160°C) and/or flame-dried glassware under atmosphere of dry argon unless otherwise noted. Chemicals used for the catalyst preparation: Nickel (II) acetate tetrahydrate, 99.99% (Sigma-Aldrich); 1,10-phenanthroline monohydrate (Alfa Aesar); Fumed silica, AEROSIL® OX 50 (Evonik Industries); Carbon powder, VULCAN® XC72R (Cabot Corporation Prod.); silicon carbide, -100 mesh (Strem); Titanium(IV) oxide, Aeroxide® P25 (Sigma-Aldrich, Ar. Nr. 718467), Cerium oxide nanopowder, <25 nm particle size (Sigma-Aldrich, Ar. Nr. 544841). Solvents: Methanol, 99% (Alfa Aesar); Etanol, 99% (Alfa Aesar); Triethylene glycol dimethyl ether, 99% (abcr GmbH) – distilled and stored over 4Å molecular sieves. The pyrolysis experiments were carried out in Nytech-Qex oven. Crucibles (height – 20 mm, top Ø – 40 mm, Ar. Nr. L219.1) and lids (Ø – 40 mm, Ar. Nr. L236.1) were purchased from Roth Industries GmbH & Co. KG.

Substrates were used as received from chemical vendors: quinaldine (TCI Europe), 1,2,3,4-tetrahydroquinaldine (TCI Europe), quinoline (TCI Europe), 1,2,3,4-tetrahydroquinoline (Sigma-Aldrich), isoquinoline (Sigma-Aldrich), 1,2,3,4-tetrahydroisoquinoline (Sigma-Aldrich), 6-methylquinoline (Sigma-Aldrich), 6-methyl-1,2,3,4-tetrahydroquinoline (abcr GmbH), 1-methyl-1,2,3,4-tetrahydroquinoline (Sigma-Aldrich), 1-acetyl-1,2,3,4-tetrahydroquinoline (abcr GmbH), 5,6,7,8-tetrahydroquinoline (Sigma-Aldrich), tetraline (Alfa Aesar), 1,2-dihydronaphthalene (Alfa Aesar).

XRD powder pattern were recorded either on a Panalytical X'Pert diffractometer equipped with a Xcelerator detector or on a Panalytical Empyrean diffractometer equipped with a PIXcel 3D detector system both used with automatic divergence slits and Cu α_1/α_2 radiation (40 kV, 40 mA; $\lambda = 0.015406$ nm, 0.0154443 nm). Cu beta-radiation was excluded by using nickel filter foil. Peak positions and profile were fitted with Pseudo-Voigt function using the HighScore Plus software package (Panalytical). Phase identification was done by using the PDF-2 database of the International Center of Diffraction Data (ICDD).

The STEM measurements were performed at 200kV with an aberration-corrected JEM-ARM200F (JEOL, Corrector: CEOS). The microscope is equipped with a JED-2300 (JEOL) energy-dispersive x-ray-spectrometer (EDXS) and an electron energy-loss spectrometer Enfinum ER (GATAN) with Dual EELS for chemical analysis. The aberration corrected STEM

imaging (High-Angle Annular Dark Field (HAADF) and Annular Bright Field (ABF)) were performed under the following conditions. HAADF and ABF both were done with a spot size of approximately 0.1nm, a convergence angle of 30-36° and collection semi-angles for HAADF and ABF of 90-170mrad and 11-22mrad respectively. The solid samples were deposited without any pretreatment on a holey carbon supported Cu-grid (mesh 300) and transferred to the microscope.

Hydrogenation experiments were carried out in 300 mL autoclave (PARR Instrument Company) in 8-mL glass vials, which were placed inside the autoclave. Dehydrogenation experiments were carried out in 25 mL Schlenk tube and hydrogen evolution was monitored using burette techniques. Reversible hydrogen storage experiments were carried out in a 25 mL autoclave (PARR Instrument Company) equipped with a mechanical stirrer.

GC Conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP5: 30 m x 250 mm x 0.25 µm. Analysis of gas samples in the dehydrogenation experiments were performed using GC HP Plot Q (FID – hydrocarbons, Carboxen / TCD - permanent gases), Ar - carrier gas. The GC was externally calibrated using certified gas mixtures from commercial suppliers (Linde and Air Liquide) with the following gas vol%:

H₂: 1%, 10%, 25%, 50%, 100%

CO: 10 ppm, 100 ppm, 250 ppm, 1000 ppm, 1%, 10%

CO₂: 1%, 50%

CH₄: 1%

The systems allow for the determination of H₂, CH₄, CO and CO₂ within the ranges:

H₂ ≥ 0.5 vol% - 100 vol%

CO ≥ 10 ppm

CO₂ ≥ 100 ppm - 100 vol%

CH₄ ≥ 1 ppm

S2. Catalyst preparation

Cats. A-D were prepared according to a previously reported procedure:¹

A 250 mL oven-dried single-necked round-bottomed flask equipped with a Allihn reflux condenser and a Teflon-coated, egg shaped magnetic stir bar (40 × 18 mm) was charged with Ni(OAc)₂·4H₂O (373.3 mg, 1.5 mmol, 1.0 equiv.), 1,10-phenanthroline monohydrate (594 mg, 3.0 mmol, 2.0 equiv.) and dissolved in ethanol (60 mL). After stirring for 5 min at 25°C, the flask was immersed in an oil bath and heated at 60°C for 2 h. To the reaction mixture 2.10 g of fumed silica (Aerosil® OX-50) or TiO₂ was added via a glass funnel and the resulting heterogeneous mixture was stirred at 750 rpm for 2 h at 60°C. The flask was taken out from the bath and cooled to ambient temperature. The solvent was removed in vacuo (180 mbar, bath temperature 40°C, 200 rpm), then dried under oil pump vacuum (1.0 mmHg, 23°C) for 14 h to give a light blue-green solid. The sample was grinded to a fine powder (2.82 g) which was then transferred to a ceramic crucible (height – 20 mm, top Ø – 40 mm) and placed in an oven. The latter was evacuated to ca. 5 mbar and then flushed with argon three times. The furnace was heated to 800 or 1000°C at a rate of 25°C per minute and held at that temperature for 2 h under argon atmosphere. After the heating was switched off the oven was allowed to reach room temperature, giving the catalyst as a black powder. (Note: during the whole process argon was constantly passed through the oven).

S3. Elemental analysis of the catalysts

Catalyst		Ni / %	N / %	C / %
Cat. A	Ni-Phen@SiO ₂ -800	3.65	1.03	14.27
Cat. B	Ni-Phen@SiO ₂ -1000	3.51	0.37	13.635
Cat. C	Ni-Phen@TiO ₂ -800	3.23	1.56	12.70
Cat. D	Ni@ SiO ₂ -1000	4.53	0	0.06
Cat. E	Ni@ SiO ₂ -800	4.65	0	0.51

¹ P. Ryabchuk, G. Agostini, M.-M. Pohl, H. Lund, A. Agapova, H. Junge, K. Junge, M. Beller, *Science Advances* **2018**, *4* : eaat0761

S4. TEM and EDX data of Cat. A after 3 hydrogenation/dehydrogenation cycles.

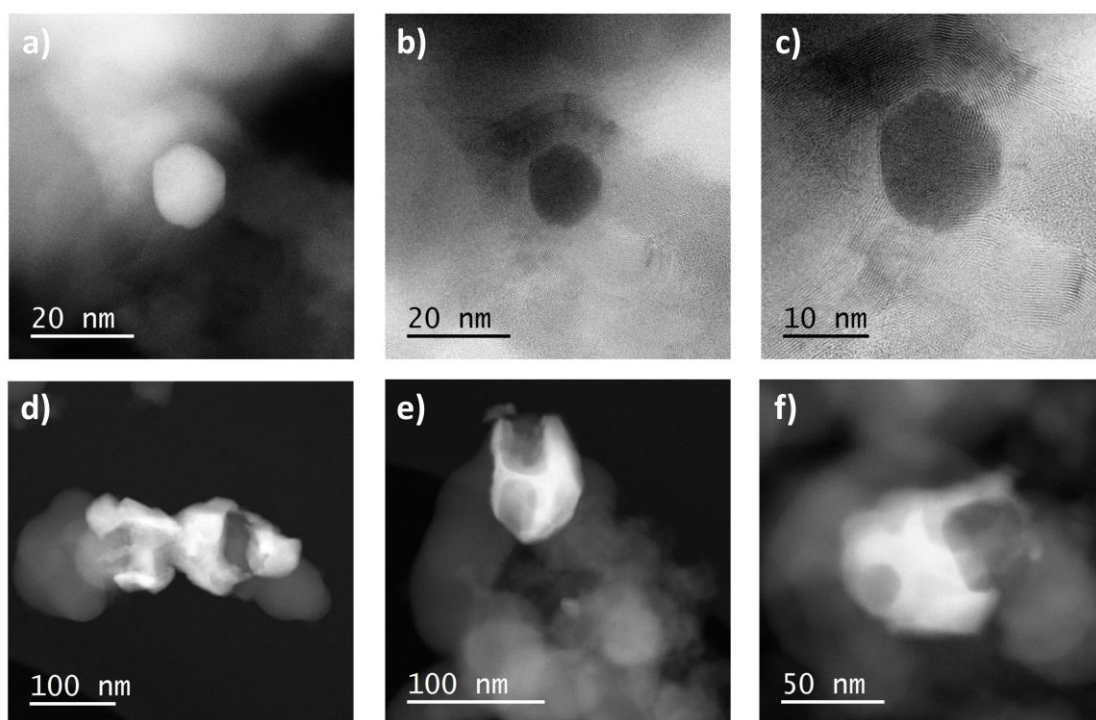


Figure. S1. ABF- and HAADF-STEM images of **Cat. A** after 3 hydrogenation-dehydrogenation cycles.

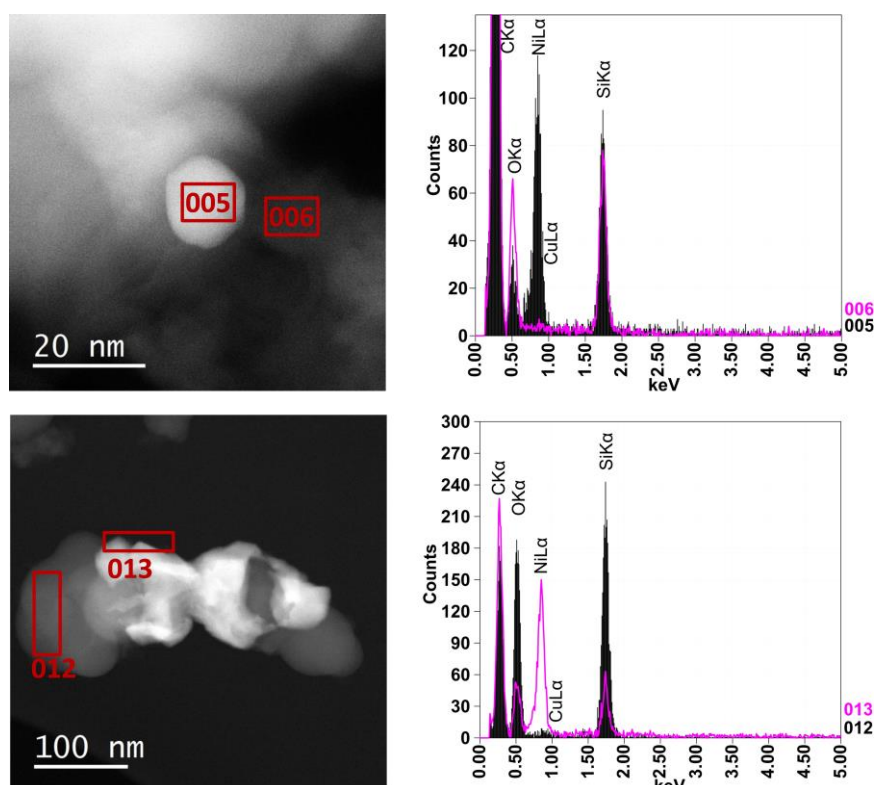


Figure. S2. HAADF-STEM and EDX measurements of **Cat. A** after 3 hydrogenation-dehydrogenation cycles.

S5. TEM and EDX data of Cat. A after 1 dehydrogenation.

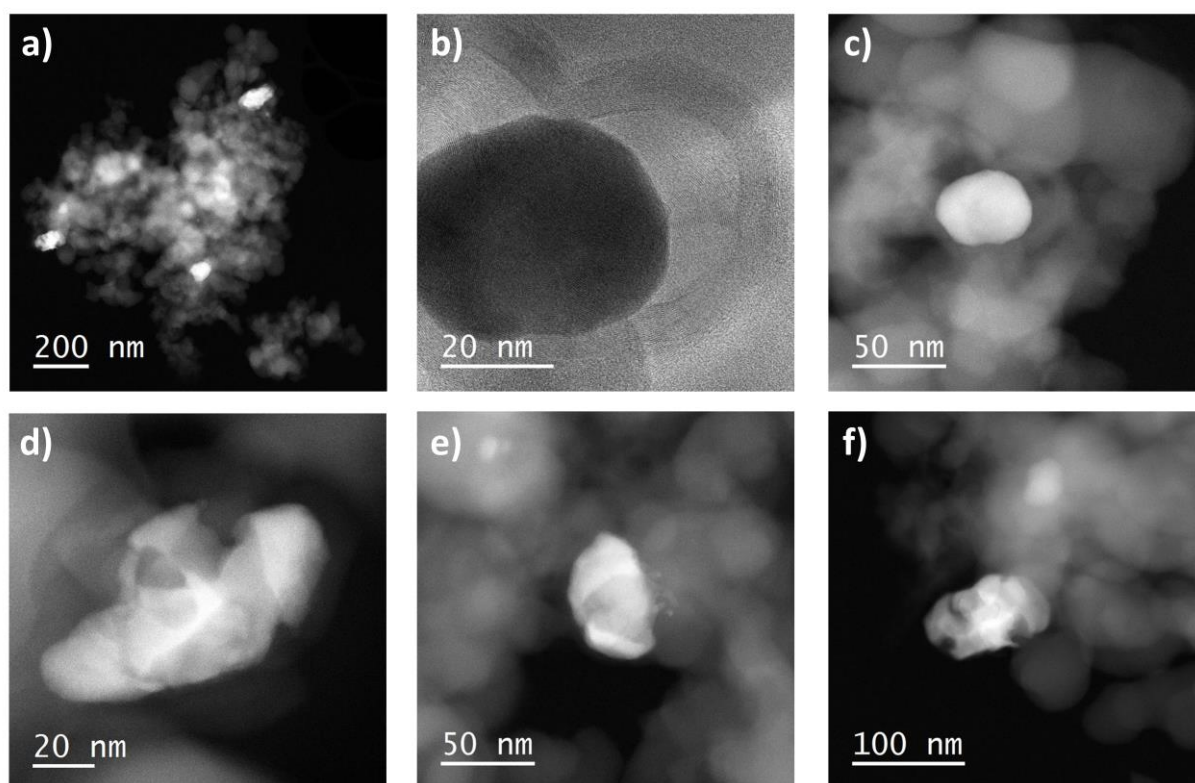


Figure. S3. ABF- and HAADF-STEM images of **Cat. A** after 1 dehydrogenation.

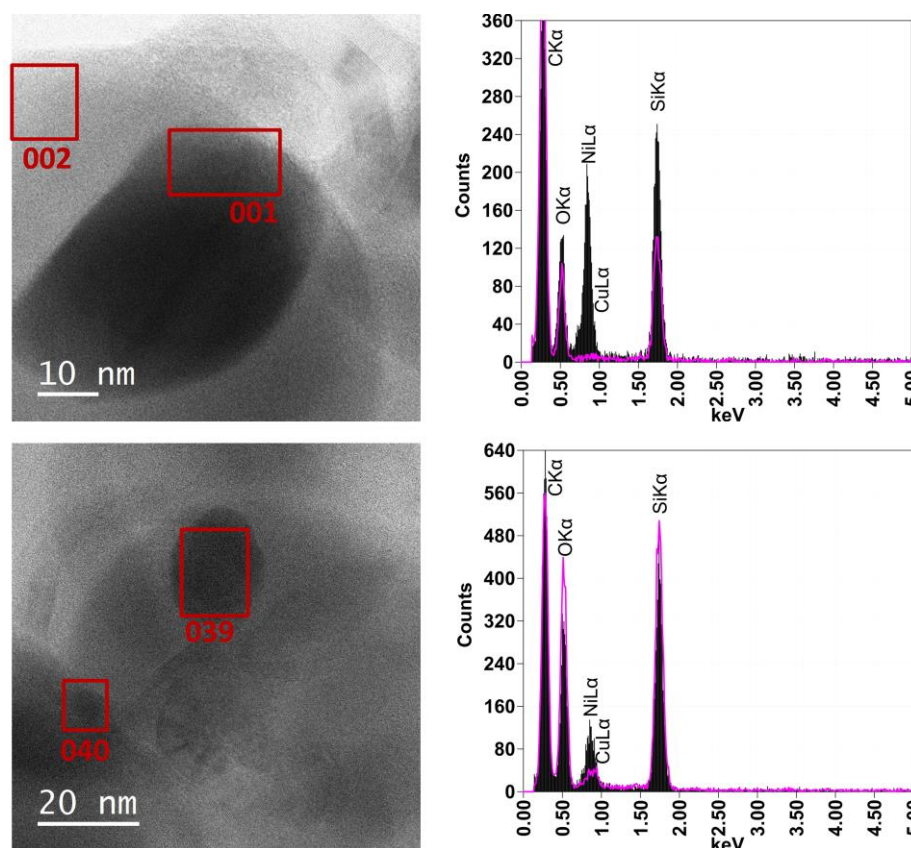


Figure. S4. ABF-STEM and EDX measurement of **Cat. A** after 1 dehydrogenation.

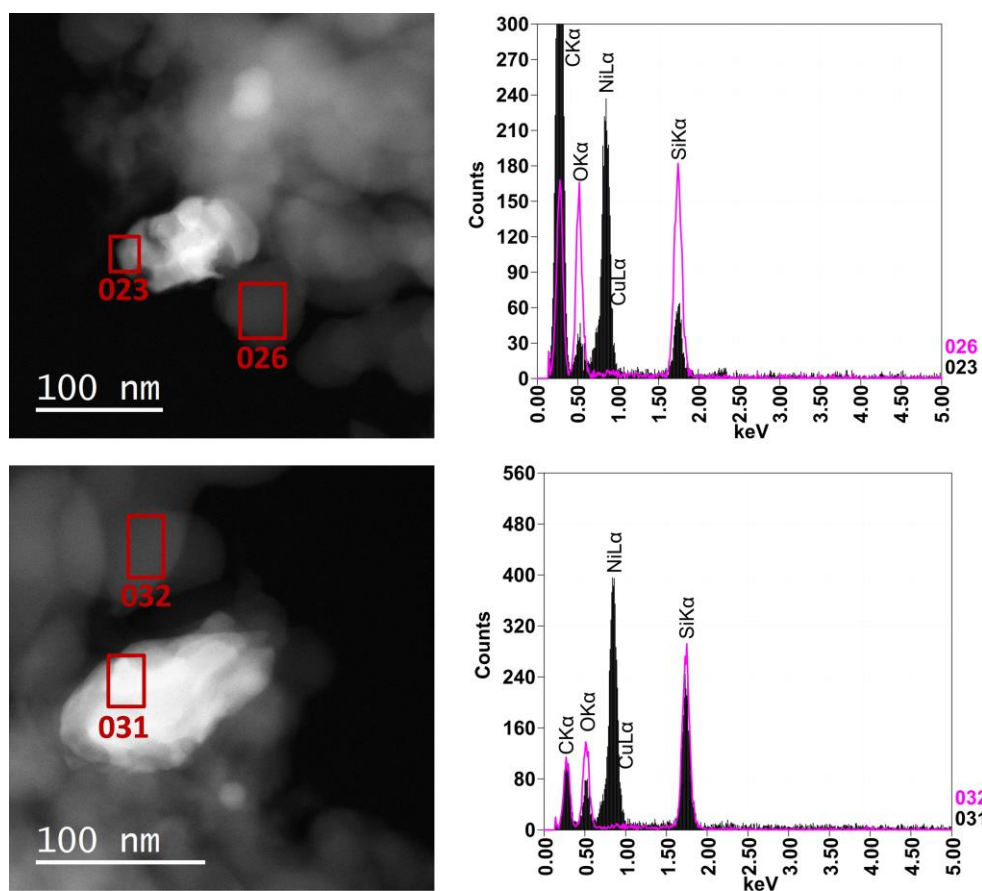


Figure. S5. HAADF-STEM and EDX measurement of **Cat. A** after 1 dehydrogenation.

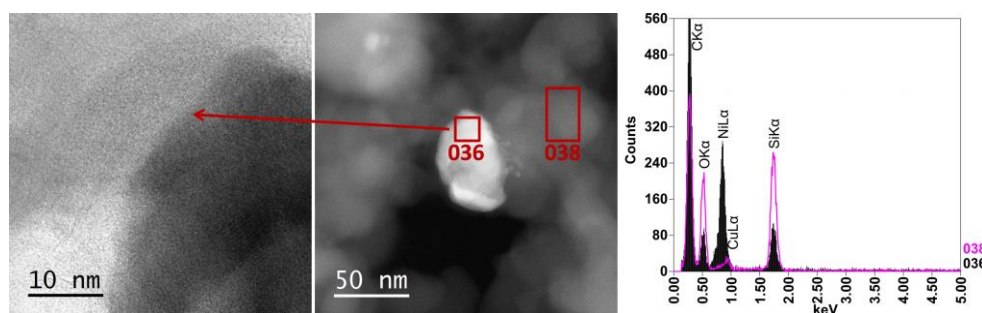


Figure. S6. ABF-, HAADF-STEM and EDX measurement of **Cat. A** after 1 dehydrogenation.

S6. TEM and EDX data of Cat. A after 1 hydrogenation.

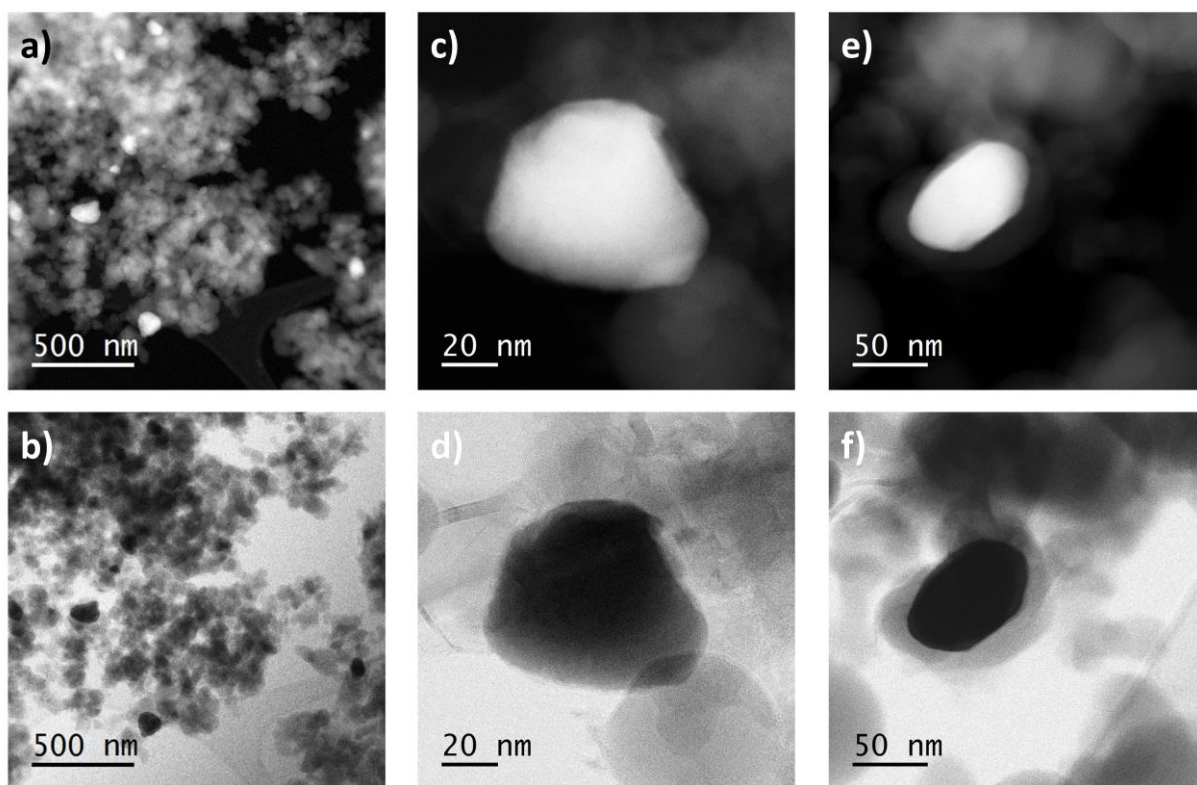


Figure. S7. HAADF-(top row) and ABF– (bottom row) images of **Cat. A** after 1 hydrogenation.

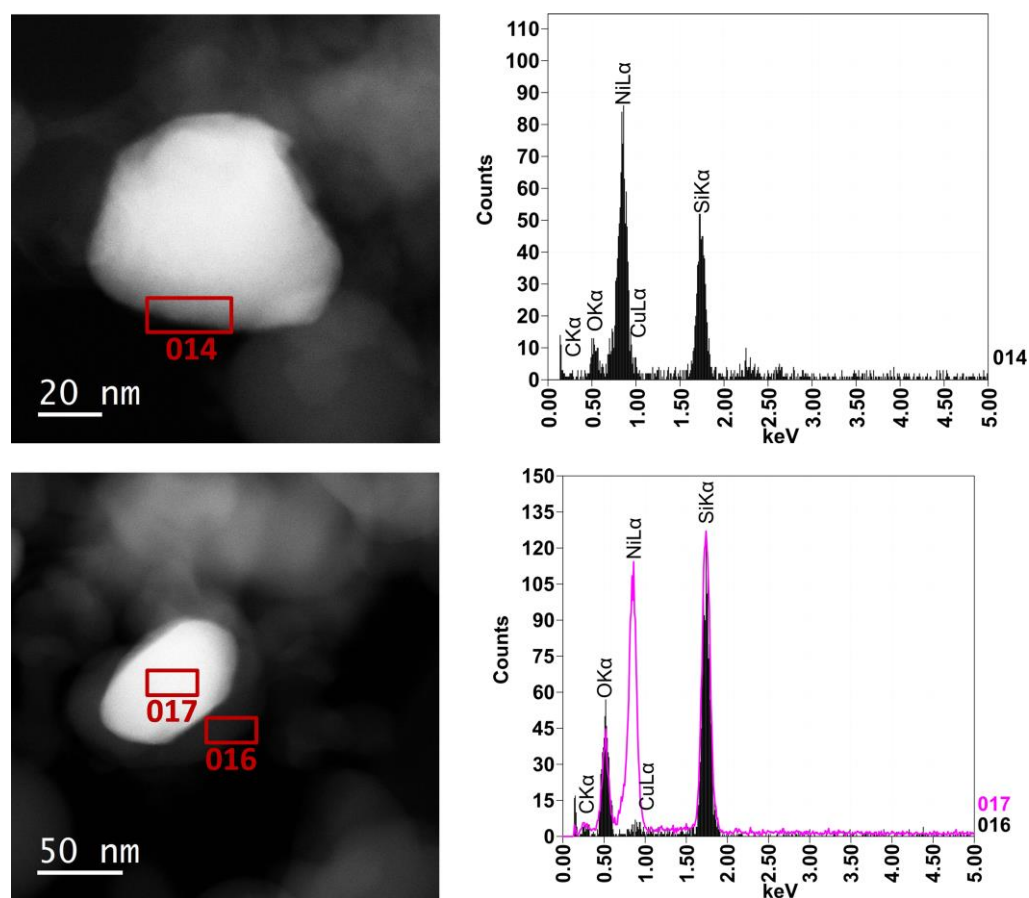


Figure. S8. HAADF-STEM and EDX measurement of **Cat. A** after 1 hydrogenation

S7. XRD Data

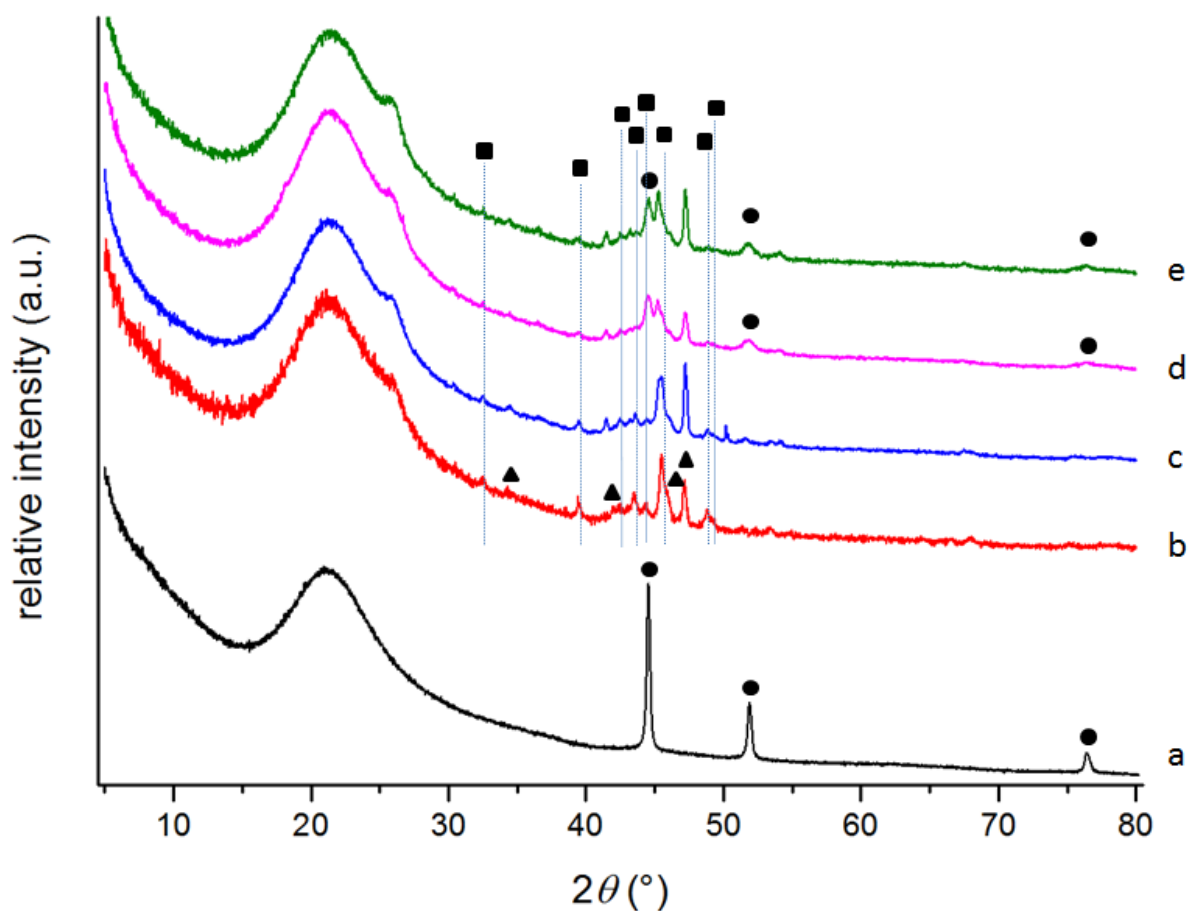


Figure S9. Powder pattern of the Ni-based catalysts: a) **Cat. D**, synthesis without ligand, b) freshly prepared **Cat. A**, c) **Cat. A** after Hydrogenation, d) **Cat. A** after Dehydrogenation and e) **Cat. A** after Recycling. Identified phases are indicated as: Ni (circle), Ni_2Si (square), $\text{Ni}_{31}\text{Si}_{12}$ (triangles).

S8. Procedures for hydrogenations

Hydrogenation of quinaldine. An 8 mL glass vial (\varnothing – 14 mm, height 50 mm) equipped with a Teflon-coated oval magnetic stirring bar (8 × 5 mm) and a plastic screw cap was charged with corresponding quinaldine (67.6 μ L, 0.5 mmol, 1.0 equiv.), 45 mg of nickel-based catalyst (\sim 4.5 mol% Ni), 1 mL of deionized water and 1 mL of methanol. The silicone septa was punctured with a 26 gauge syringe needle (0.45 × 12 mm) and the vial was placed in placed in the aluminum plate which was then transferred into the 300 mL autoclave. Once sealed, the autoclave was placed into an aluminium block and purged 3 times with hydrogen (at 5-10 bar). Then it was pressurized to 30 bar, heated up and kept at 120°C under thorough stirring (700 rpm). After 16 h, the autoclave was removed from the aluminum block and cooled to room temperature in a water bath. The remaining hydrogen was discharged and the vials containing reaction products were removed from the autoclave. To the crude reaction mixture 100 μ L of n-hexadecane (internal standard) was added, followed by the addition of 6 mL of ethyl acetate. The resulting mixture was intensively stirred for 30 seconds and then the solid catalyst was separated by centrifugation and the liquid phase was subjected to GC analysis.

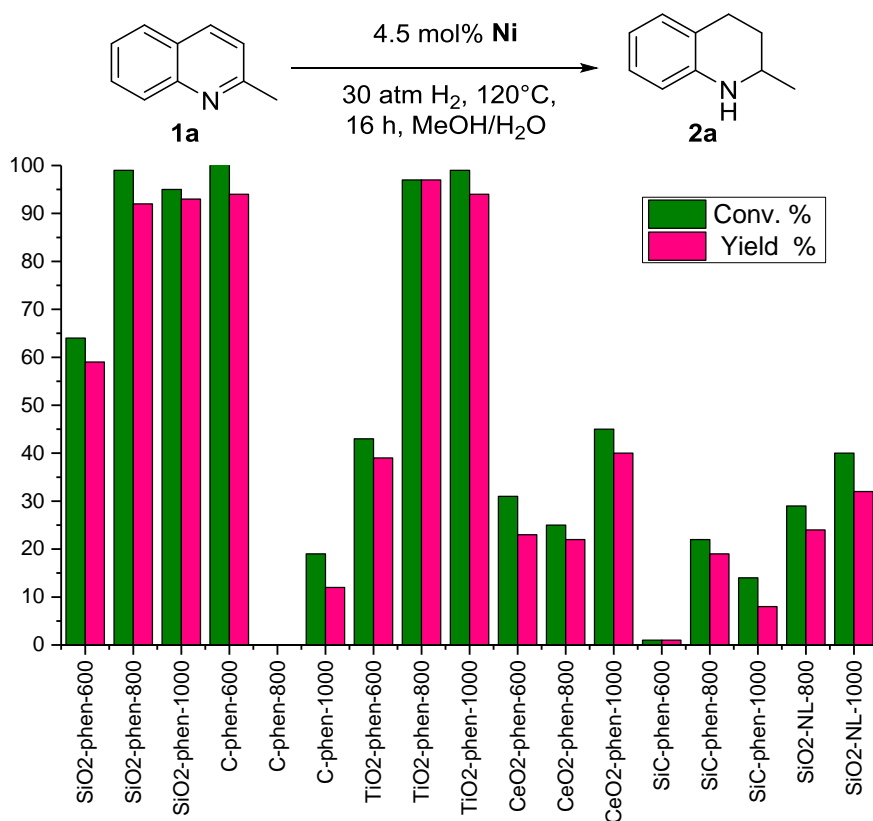


Table S1 Hydrogenation of quinaldine with various Ni-based catalysts at 30 bar H₂.

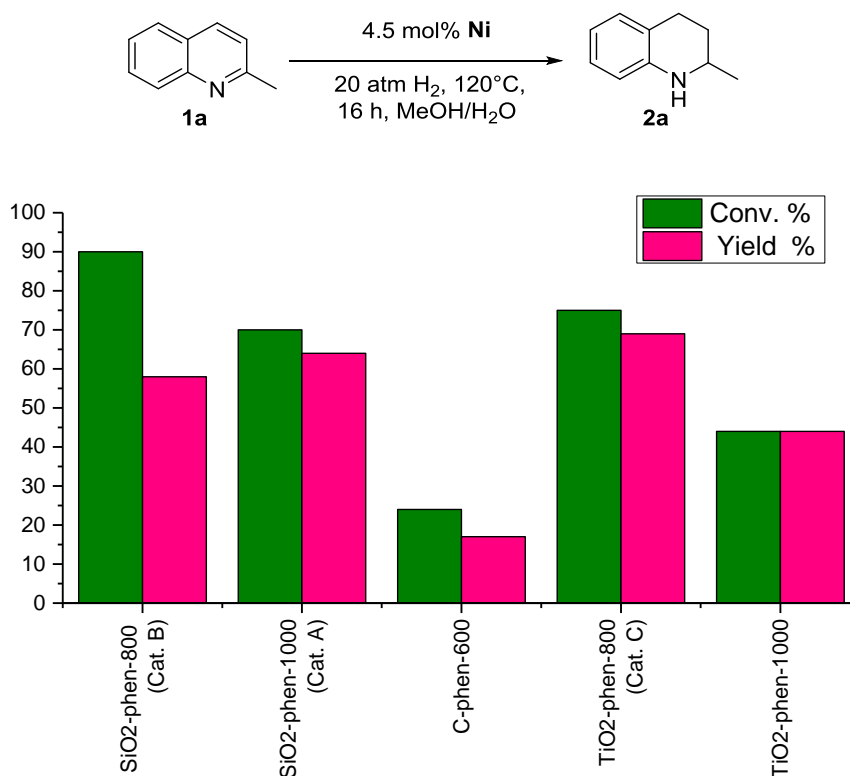


Table S2 Hydrogenation of quinaldine with various Ni-based catalysts at 20 bar H₂.

Entry	Substrate	Product	Yield, (Conv.)% ^[a]
1	<chem>Cc1ccc2nc3ccccc3n2</chem> 1a	<chem>Cc1ccc2cnc3ccccc32</chem> 2a	93 (95)
2	<chem>Cc1ccc2cnc3ccccc32</chem> 1b	<chem>Cc1ccc2cnc3ccccc32</chem> 2b	86 (97)
3	<chem>Cc1ccc2cnc3ccccc32</chem> 1c	<chem>Cc1ccc2cnc3ccccc32</chem> 2c	50 (75)
4	<chem>Cc1ccc2cnc3ccccc32</chem> 1d	<chem>Cc1ccc2cnc3ccccc32</chem> 2d	99 (100)

Table S3. Hydrogenation of N-heterocycles in the presence of Cat. A in MeOH/H₂O. Conditions: **1** (0.5 mmol), 45 mg of **Cat. A** (4.5 mol%), 2 mL MeOH/H₂O (1:1), 30 bar H₂, 16h.; [a] Yields and conversions were determined by GC analysis of the liquid phase, using n-hexadecane as the internal standard

S9. Procedures for dehydrogenations

Dehydrogenation of 1,2,3,4-tetrahydroquinoline: A 25 mL Schlenk tube was charged at ambient atmosphere with Ni catalyst (500 mg for **Cat. A-C** or 300 mg for **Cat. D** and **Cat. E**, 20 mol% Ni), 1,2,3,4-tetrahydroquinoline (180 μ L, 1.25 mmol, 1.0 equiv.). The Schlenk tube was connected to the reaction setup and the whole system was flushed with Ar for 20 minutes, followed by the heating to 200°C in aluminum block. The desired temperature was achieved within 20 min. The measurement of the gas evolution was started together with starting the heating. The influence of temperature on the volume was corrected by performing reactions without a catalyst (See calculation of conversion). After running the reaction for the desired time, a gas sample was taken to determine the identity and quantity of the gas components. Every reaction was performed at least twice, the standard deviation divided by the average value * 100% is in between 1 and 10 %.



Figure S10. Manual burette setup used in this study.

Calculation of conversion

The measured gas volumes were corrected by a blank volume (gas evolution measured in a reaction performed without catalyst under the same conditions).

The gas production was calculated by the equation **(S1)**:

$$\text{Gas production} = V_{obs} - V_{blank} \quad (\text{S1})$$

where V_{obs} and V_{blank} are the gas volume measured in the catalytic reaction and the blank reaction, respectively. Conversion was calculated by the equation **(S2)**:

$$\text{Conversion} = \frac{V_{obs} - V_{blank}}{V_{m,H_2,25^\circ C} * n_{H_2expected}} \quad (\text{S2})$$

The calculation of $V_{m,H_2,25^\circ C}$ was carried out using Van der Waals equation **(S3)**:

$$V_{m,H_2,25^\circ C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48 \frac{L}{mol} \quad (\text{S3})$$

Where:

$$R: 8.3145 \text{ m}^3 \cdot \text{Pa} \cdot \text{mol}^{-1} \cdot \text{K}^{-1};$$

$$T: 298.15 \text{ K};$$

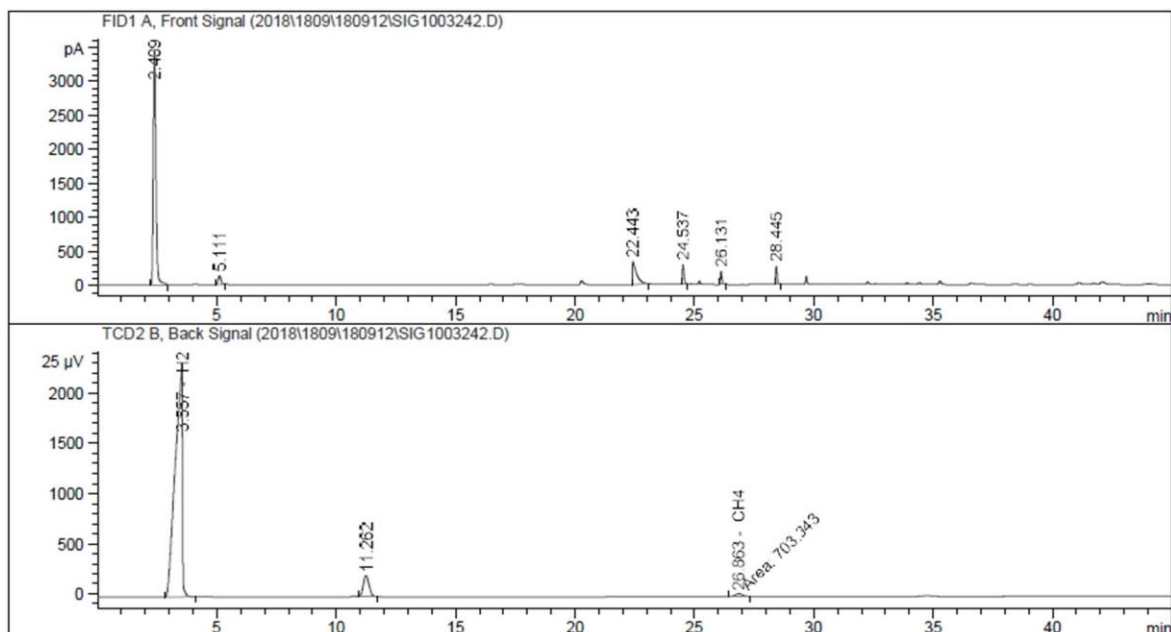
$$P: 101325 \text{ Pa};$$

$$a: 24.7 \cdot 10^{-3} \cdot \text{Pa} \cdot \text{m}^6 \cdot \text{mol}^{-2};$$

$$b: 26.6 \cdot 10^{-6} \text{ m}^3 \cdot \text{mol}^{-1}$$

GC analysis

An example of the resulting GC is shown below (Fig S10). FID signal (retention time 28.39 min) in the upper part shows the substrate (1,2,3,4-tetrahydroquinoline), which is in the vapor phase. The contribution of this compound to the overall volume is equalized by correction with the blank volume. Peak 11.262 min is caused by air leaked in the gas syringe.



External Standard Report

Sorted By : Signal
 Calib. Data Modified : 2/20/2018 2:27:26 PM
 Multiplier : 1.0000
 Dilution : 1.0000
 Use Multiplier & Dilution Factor with ISTDs

Signal 1: FID1 A, Front Signal

Signal 2: TCD2 B, Back Signal

RetTime [min]	Type	Area [25 µV*s]	Amt/Area	Amount [% Vol.]	Grp	Name
3.557	BB	4.82540e4	3.18103e-4	15.34976	H2	
14.700		-	-	-	CO	
26.863	MM	703.34271	6.31574e-4	4.44213e-1	CH4	
34.271		-	-	-	CO2	

Figure S11. Gas composition analysis by GC.

Dehydrogenation of other N-Heterocycles: A 25 mL Schlenk tube was charged at ambient atmosphere with **Cat. A** (500 mg, 20 mol% Ni), N-heterocycle (1.25 mmol, 1.0 equiv.). The Schlenk tube was connected to the reaction setup and the whole system was flushed with Ar for 20 minutes, followed by the heating to 200°C in aluminum block. The desired temperature was achieved within 20 min. The measurement of the gas evolution was started together with starting the heating. The influence of temperature on the volume was corrected by performing reactions without a catalyst (See calculation of conversion). After running the reaction for the desired time, a gas sample was taken to determine the identity and quantity of the gas components. Every reaction was performed at least twice, the standard deviation divided by the average value * 100% is in between 1 and 10 %.

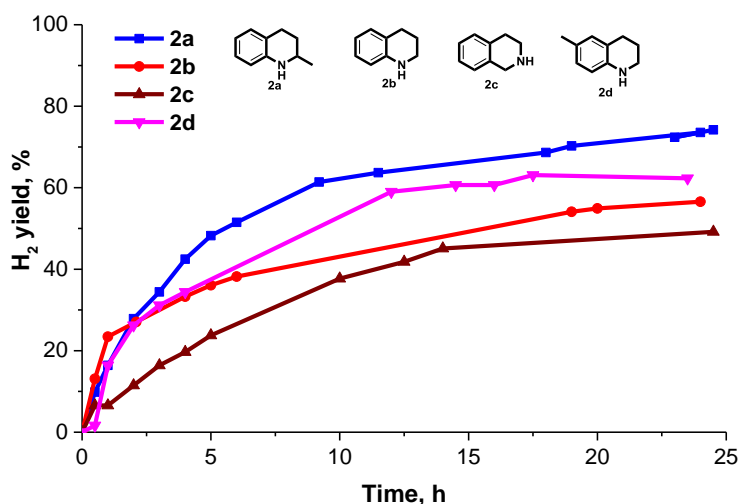


Figure. S12. Dehydrogenation of N-heterocycles in the presence of Cat. A. Conditions: 2 (1.25 mmol), 500 mg of Cat. A. (20 mol%), 5 mL triglyme, Ar. GC analysis of the liquid phase was in good agreement with the amount of hydrogen gas evolved, deviation did not exceed 3% in each case.

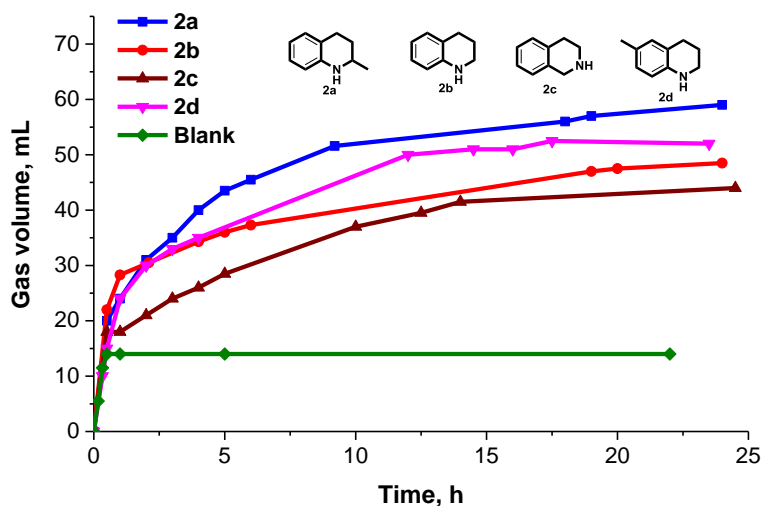


Figure. S13. Gas evolution from N-heterocycles in the presence of Cat. A. Original data is measured for the hydrogen evolution from the substrate. The volumes are not corrected by blank volume.

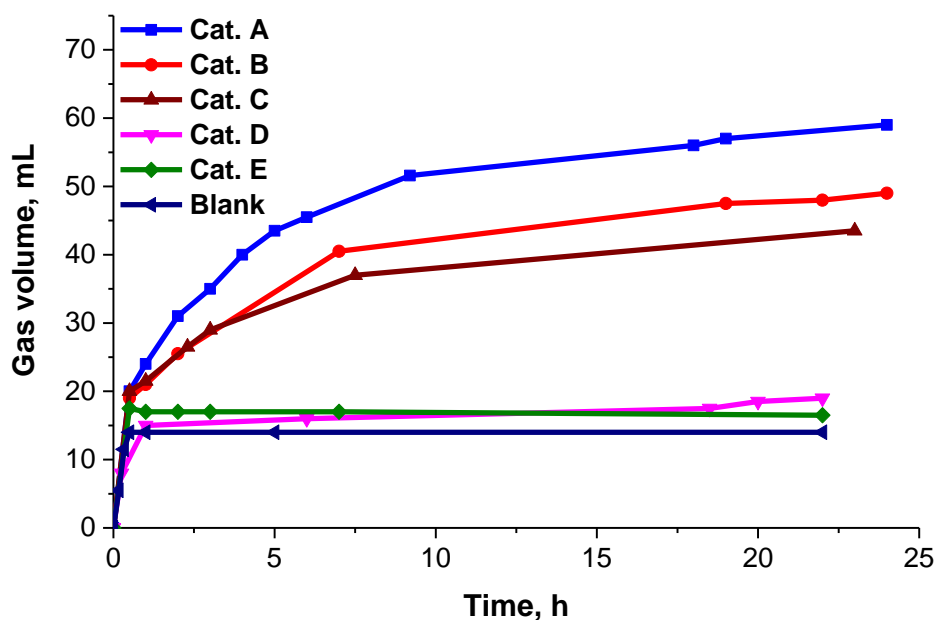
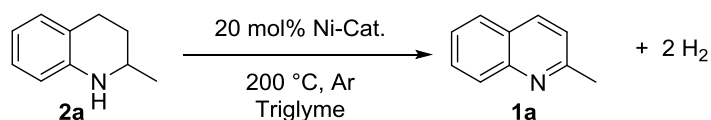


Figure. S14. Dehydrogenation of 2a in the presence of Cat. A-E. Conditions: 2a (1.25 mmol), 300-500 mg of Ni-Cat. (20 mol%), 5 mL triglyme, Ar; Original data is measured for the hydrogen evolution from the substrate. The volumes are not corrected by blank volume.

S10. Procedure for catalyst recycling

Hydrogenation-Dehydrogenation Cycle: A 25 mL autoclave (PARR Instrument Company) equipped with a mechanical stirrer was charged with **Cat. A** (500 mg, 20 mol% Ni), **1a** quinaldine (169 μ L, 1.25 mmol, 1.0 equiv.). The autoclave was sealed and purged with hydrogen (at 5-10 bar). Then it was pressurized with 50 bar H₂, heated up to 120°C under thorough stirring (700 rpm). After 16 h, the autoclave was removed from the aluminum block and cooled to room temperature in a water bath. The remaining hydrogen was discharged and the reaction mixture was analyzed by GC. Then the autoclave was sealed and flushed with Ar for 20 minutes, followed by the heating to 200°C in aluminum block under thorough stirring (700 rpm). After 24 h, the autoclave was cooled to room temperature and the formed gas was released, followed by additional heating for 24 h at 200°C. The autoclave was cooled, degassed and the reaction mixture was analyzed by GC. This procedure was repeated three times.