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

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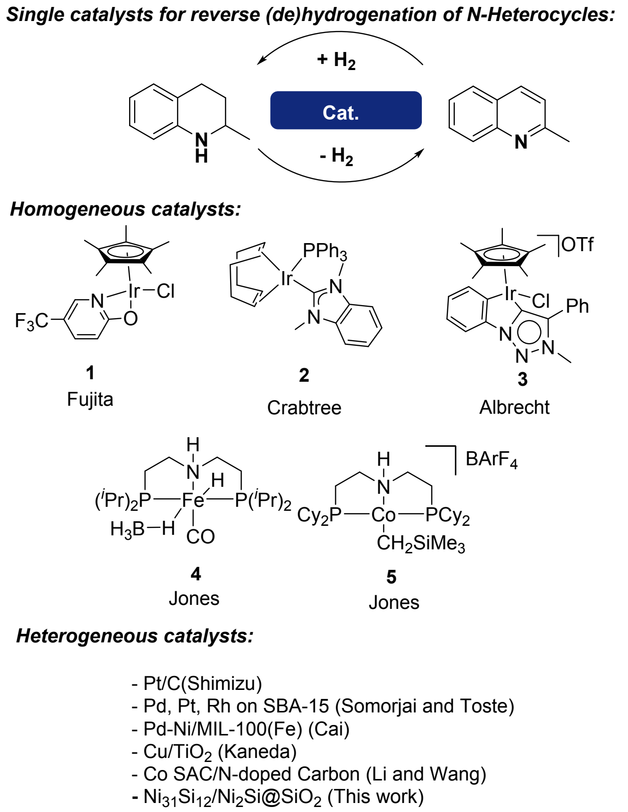
Pavel Ryabchuk, Anastasiya Agapova, Carsten Kreyenschulte, Henrik Lund, Henrik Junge, Kathrin Junge and Matthias Beller*

Nickel-based nanocatalysts were used in acceptorless, reversible dehydrogenation and hydrogenation reactions of N-heterocycles. Both processes were realized in the same solvent using a single catalyst, without isolation of products and workup, which makes it attractive for hydrogen storage purposes. This concept has been demonstrated in a continuous hydrogenation/dehydrogenation sequence of quinaldine with negligible loss in activity of the nickel catalyst after three hydrogen storage cycles. The scope of acceptorless dehydrogenation has been explored and control experiments suggest that hydrogen liberation is initiated via amine dehydrogenation and support the direct alkane dehydrogenation from the partially oxidized N-heterocycles.

Catalytic acceptorless dehydrogenations (CADs) are an important class of reactions that transform the substrate by liberation of hydrogen gas. In terms of atom economy and waste generation this approach has obvious advantages compared to traditional methods using stoichiometric amounts of oxidant or sacrificial hydrogen acceptors.[1] Hence, apart from synthetic applications, CADs have attracted attention from the point of “hydrogen economy”, which is a key technology for chemical hydrogen storage.[2] Among various liquid organic hydrogen carriers (LOHCs), nitrogen-containing heterocycles, such as quinolines, are particularly attractive for hydrogen storage.[3] According to experimental and computational studies the presence of the nitrogen atom in heterocycles significantly decreases the ΔH^0 of dehydrogenation, compared to their corresponding cycloalkanes.[4] Despite significant progress in the development of catalytic hydrogenations[5] and dehydrogenations[1] of N-heterocycles, systems that utilize a single catalyst for both processes are extremely rare.[6,7]



Scheme 1. Single catalysts for acceptorless dehydrogenation and hydrogenation of N-heterocycles.

The first catalytic system for the reversible dehydrogenation/hydrogenation of quinoline derivatives using iridium-based complex **1** was reported by Fujita and co-workers in 2009. In the past decade a number of homo- and heterogeneous catalysts has been developed, however most of them rely on noble metals, such as Ir, Pt, Pd, and Rh. (Scheme 1). In two cases, high levels of activity were achieved using earth abundant metal-based homogeneous catalysts, namely iron and cobalt. Molecular pincer complexes **4** and **5**, studied by the group of Jones, are very attractive, but they are air- and moisture sensitive and require more expensive ligands. Development of heterogeneous catalysts based on

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[a] Leibniz-Institut für Katalyse e. V. an der Universität Rostock
[b] Albert-Einstein-Straße 29a, 18059 Rostock
[c] E-mail: matthias.beller@catalysis.de

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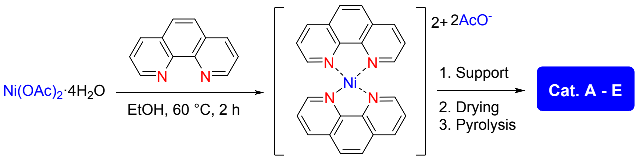
non-noble metals is highly desired, yet only two catalytic systems of this kind are known.

Cu nanoparticles supported on TiO_2 reported by Kaneda, have been used for hydrogenation/dehydrogenation of quinoline, however besides high metal loading this catalyst requires additional activation with H_2.[7d] Recently, a cobalt single atom catalyst (SAC) stabilized on a nitrogen-doped carbon matrix has been developed by the group of Wang and Li.[7e] This material showed good activity, but it was not tested in the consecutive hydrogenation/dehydrogenations of N-heterocycles, leaving space for improvements. Besides harsh reaction conditions and extended reaction times, most of the known catalysts require different solvents for hydrogenation and dehydrogenation steps. For practical reasons, both hydrogen uptake and release ideally should occur in the presence of the same catalyst in the same reaction.

Therefore, as a part of an ongoing research program utilizing first-row metal based heterogeneous catalysts for (de)hydrogenation reactions, we became interested in development of nickel-based heterogeneous catalysts, which can be used for hydrogen storage in N-heterocycles. To the best of our knowledge, catalysts solely based on nickel have not been used in this type of system. In general, nickel is used much more frequently for hydrogenations, than for hydrogen release. So far, the scope for the latter is limited to dehydrogenations of alcohols,[8] ammonia borane,[9] hydrocarbons,[10] and dehydrogenative coupling reactions with alcohols.[11] Herein, we report an intermetallic nickel silicide catalyst supported on fumed silica (AEROSIL® OX 50), which promotes the hydrogenation/dehydrogenation of N-heterocycles.

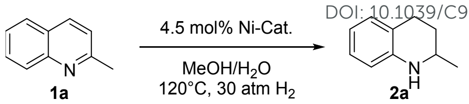


Ni-Cat.	Pyrolysis T., C°	Ligand	Support
Cat. A	1000	1,10-phenanthroline	SiO_2
Cat. B	800	1,10-phenanthroline	SiO_2
Cat. C	800	1,10-phenanthroline	TiO_2
Cat. D	1000	None	SiO_2
Cat. E.	800	None	SiO_2

Scheme 2. Preparation of nano-structured Ni-based catalysts studied in this work.

The catalyst was prepared via impregnation of molecularly-defined nickel phenanthroline complexes on fumed silica support and subsequent pyrolysis at 1000°C.[12] The resulting material (**Cat. A**) consists of a $Ni_2Si/Ni_{31}Si_{12}$ core and NiO/SiO_2 shell, covered with N-doped graphene layers: Ni-Si/NiO-SiO_2@SiO_2 (Scheme 1). **Cat. A** catalysed hydrogenation of a variety of substrates, including olefins, alkynes, nitroarenes, ketones and aldehydes, while the dehydrogenations were studied to a lesser extent.

Table 1. Hydrogenation of quinaldine.[a]



Entry	Ni-Cat.	Conv., %[b]	Yield, %[b]
1	**Cat. A**	95	93
2	**Cat. B**	>99	92
3	**Cat. C**	97	96
4	**Cat. D**	29	24
5	**Cat. E.**	40	32

[a]Conditions: 1a (0.5 mmol), 40-45 mg of Ni-Cat. (4.5 mol%), 2 mL MeOH/H_2O (1:1), 30 bar H_2, 16h. [b] Yields and conversions were determined by GC analysis of the liquid phase, using *n*-hexadecane as the internal standard.

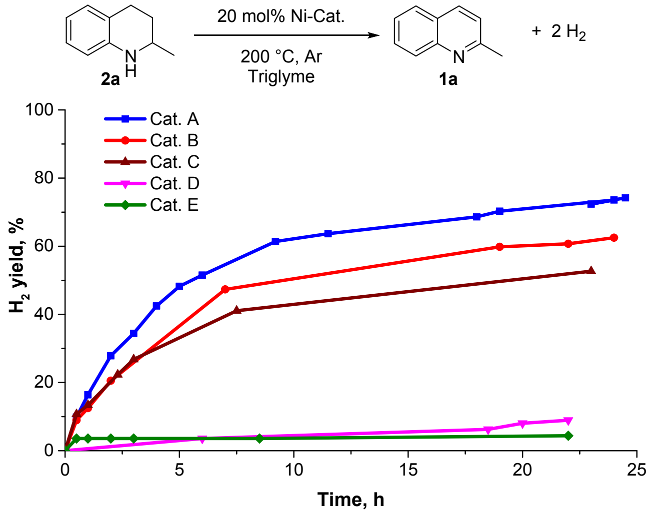


Figure 1. Dehydrogenation of **2a** in the presence of **Cat. A-E.** Conditions: **2a** (1.25 mmol), 300-500 mg of Ni-Cat. (20 mol%), 5 mL triglyme, Ar; H_2 production was measured with a manual burette.[13]

Inspired by our preliminary results, we started a systematic investigation in order to find an efficient catalyst that can be used for both hydrogenation/dehydrogenation of quinoline derivatives. Initially, a number of nickel-based materials were prepared in a similar fashion named Ni–Ligand@Support–Tpyrolysis according to the procedure (Scheme 2).

Among these materials, Ni-phen@SiO_2-800 (**Cat. B**) and Ni-phen@TiO_2-800 (**Cat. C**) were identified showing comparable activity to **Cat. A** for the hydrogenation of quinaldine (Table 1, see also Table S1). Thus, these three Ni-based catalysts (**Cat. A-C**) were examined regarding their efficiency in the reverse dehydrogenation of **2a**. The catalyst activity was evaluated by measuring the volume of evolved hydrogen gas (Figure 1). After 24h at 200°C in triglyme, **Cat. A** gave 74% yield of H_2, whereas **Cat. B** and **Cat. C** showed reduced activity reaching 63% and 53% yield, respectively. The identity of the released hydrogen was confirmed by GC, with 0.5% of CO_2 and trace amounts of CO and CH_4 present (< 0.1% each). In our previous studies on iron[14] and cobalt[15] nanocatalysts, we demonstrated that the presence of an N-containing ligand in the preparation step has a great impact on the catalytic activity. To examine

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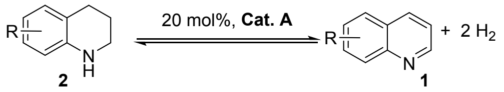
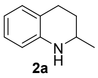
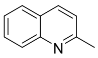
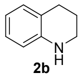
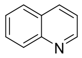
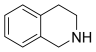
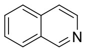
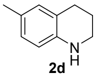
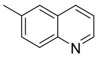
the role of 1,10-phenanthroline on the hydrogenation /dehydrogenation of **1a**, **Cat. D** and **E** prepared in the absence of ligand were tested. Interestingly, both materials gave only partial hydrogenation of **1a** (Table 1, entries 4 and 5) and failed to catalyse the reverse dehydrogenation of **2a**. Next, the substrate scope of (de)hydrogenation of N-heterocycles was studied in the presence of **Cat. A** (Table 2).

Table 2. (De)hydrogenation of N-heterocycles with **Cat. A**.[a]



Substrates		**Dehydrog.:** H_2 Yield, % [b]	**Hydrog.:** Yield, (Conv.)% [d]
 **2a**	 **1a**	74 (93[c])	93 (100)
 **2b**	 **1b**	57	91 (100)
 **2c**	 **1c**	50	NA[e] (80)
 **2d**	 **1d**	62	92 (100)

[a] Dehydrogenation: **2** (1.25 mmol), 500 mg of **Cat. A** (20 mol%), 200°C, 24 h. 5 mL triglyme, Ar.; Hydrogenation: **1** (0.25 mmol), 100 mg of **Cat. A** (20 mol%), 2 mL triglyme, 120°C, 50 bar H_2, 16h; [b] H_2 production was measured with a manual burette; [c] H_2 production measured after 48 hours [d] Yields and conversions were determined by GC analysis of the liquid phase, using *n*-hexadecane as the internal standard; [e] NA = not available, GC signal for **2c** overlaps with triglyme.

Dehydrogenation of various heterocycles was monitored by gas evolution in the first 24 h of the reaction. Tetrahydroquinaldine **2a** gave 74% of the maximum hydrogen quantity, while homologous **2b** reached only 57%. The methyl substitution of the aromatic ring in **2d** resulted in increased hydrogen evolution: 62% after 24 h. Notably, 1,2,3,4-tetrahydroisoquinoline **2c** showed the lowest rate, reaching only 50% conversion after 24 hours. As shown above, complete conversion of **1a** to **2a** can be achieved with 4.5 mol% **Cat. A** at 30 bar H_2 in methanol-water mixture, however hydrogenation in triglyme requires higher hydrogen pressure and catalyst loading. With exception of **1c**, all N-heterocycles can be fully hydrogenated both in methanol-water and triglyme. Based on the rate of dehydrogenation of **2a**, **1a**/**2a** were selected as model substrates for hydrogen storage. Initial hydrogenation of **1a** was performed in triglyme using 20 mol% of **Cat. A** in a steel autoclave with a mechanical stirrer. Upon completion of the reaction, without workup or any other manipulations, the obtained product **2a** was dehydrogenated at 200 °C in the same autoclave. The hydrogen uptake/release was demonstrated for three consecutive cycles with no loss in reactivity (Figure 2). Although atomic absorption spectroscopy (AAS) revealed no measurable leaching after a single (de)hydrogenation step, upon three consecutive cycles small amounts of nickel were detected in solution (~20 ppm).

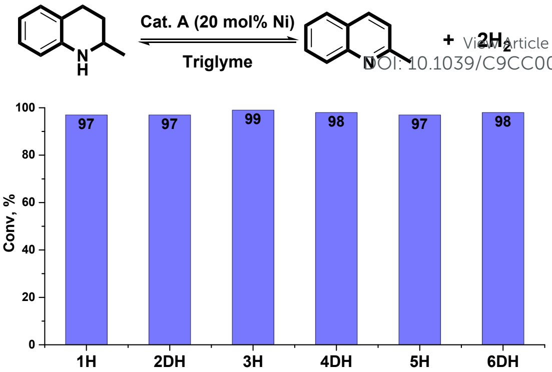


Figure 2. Catalyst reusability and reversible hydrogen storage with **1a** (1.25 mmol), 500 mg **Cat. A** (20 mol% Ni), 5 mL triglyme. Hydrogenation (H): 120°C, 50 bar H_2, 16h Dehydrogenation (DH); 200°C, Ar, 48h. The hydrogen uptake and release values were calculated by GC analysis of the liquid phase of **1a** and **2a** and based on the preceding step.

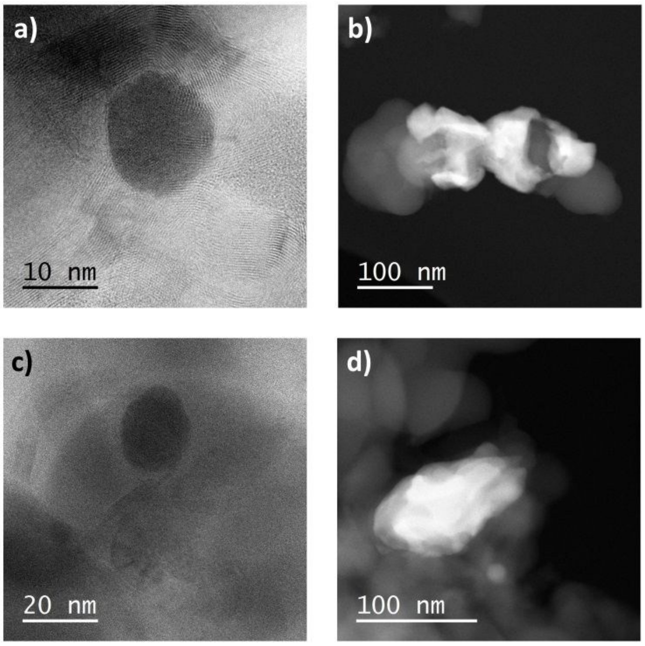


Figure 3. (a,b) STEM images of **Cat. A** after 3 hydrogenation-dehydrogenation cycles. The annular bright field (ABF) image (a) shows the presence of nanoparticles covered by a graphitic structure, while high angle annular dark field (HAADF) image (b) displays metallic Ni particles with irregular shape. STEM images (c,d) of **Cat. A** after a single dehydrogenation, demonstrate the presence of similar metallic Ni particles (d), while also some nanoparticles graphite-covered are present (c).

Even though **Cat. A** showed no noticeable deactivation after 3 cycles, analysis of the material revealed structural changes in the catalyst. STEM images of **Cat. A** were acquired at different stages and are shown in Figure 3 (Figures S1-S8). Apart from nickel nanoparticles covered by a graphitic structure (a), large metallic nickel particles with irregular shapes were formed (b). Intrigued by these unexpected changes in the material structure compared to the fresh catalyst[12], we examined **Cat. A** after a single hydrogenation of **1a** and a single dehydrogenation of **2a**. Upon hydrogenation,

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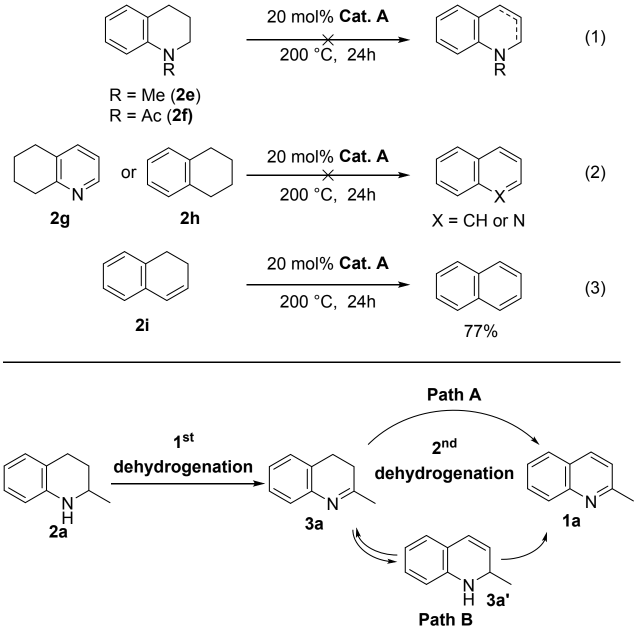
nickel silicide particles remained, as judged by XRD (Figure S9), and no strongly irregular-shaped Ni(0) particles were formed (Figures S7, S8) although quite compact Ni(0) particles were present. Relatively large and irregular shaped Ni(0) appeared only after or during the dehydrogenation process (Figure 5(d), Figures S3-S6). Since no significant loss in activity has been observed, we suggest that these Ni(0) particles are catalytically active for the (de)hydrogenation of N-heterocycles.



Scheme 3. Control experiments and proposed reaction mechanism.

To get insights into the mechanism of nickel-catalysed dehydrogenation of heterocycles, control experiments with selected substrates have been performed (Scheme 3). Two substrates bearing a protected nitrogen atom **2e** and **2f** do not react in the dehydrogenation (eq 1). These results clearly show the important role of a free N-H group in the dehydrogenation process. Moreover, isomeric 5,6,7,8-tetrahydroquinoline **2g** with no saturated C-N bonds failed to produce **1b**. As expected, a carbon analogue tetraline **2h** does not react under optimized reaction conditions. However, 1,2-dihydronapthalene **2i** yield 77% of naphthalene. Based on the results above, we propose, that the dehydrogenation sequence starts with the release of one equivalent of H_2, from the C-N bond, giving intermediate **3a**. Further dehydrogenation can proceed in two different scenarios: via direct alkane dehydrogenation (Path A) or via tautomerization to **3a'** and subsequent dehydrogenation from the secondary amine fragment as postulated by Jones (Path B). Based on the activity of **2i**, which is structurally relevant to **3a**, direct dehydrogenation of **3a** to **1a** via Path A is possible. We believe that the liberation of the second equivalent of H_2 occurs via both reaction pathways.

In summary, we demonstrated the first heterogeneous nickel nanostructured catalyst (**Cat. A**) capable of promoting hydrogenation and dehydrogenation of N-heterocycles. This robust, reusable, and highly efficient material allows for hydrogen storage in quinoline derivatives. The hydrogen uptake/release was demonstrated for three consecutive cycles under optimized conditions. Preliminary mechanistic studies are evident of the initial amine-dehydrogenation step and support the direct alkane dehydrogenation from the partially oxidized N-heterocycles.

Conflicts of interest

There are no conflicts to declare.

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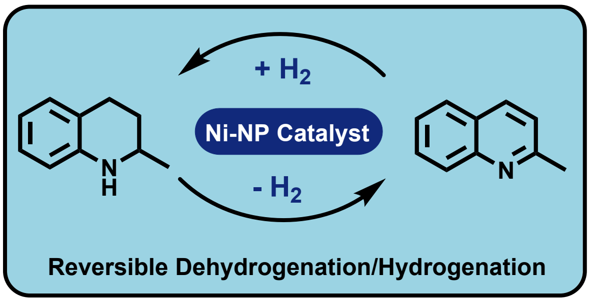

Nickel catalyst for hydrogen storage in N-heterocycles: A heterogeneous nickel catalyst promotes both hydrogenation and subsequent dehydrogenation of quinoline derivatives.