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A Highly Active Nickel Catalyst for the Selective Hydrogenation of Functionalized Nitroarenes

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Dedicated to Prof. Michael Ruck on the occasion of his 60th birthday

The catalytic hydrogenation of nitroarenes using hydrogen gas as reducing agent to form substituted aniline derivates is an important reaction in industry and academic research. Here, we report on the nitroarene hydrogenation capability of a nano-structured nickel catalyst synthesized from a nickel salen complex and a commercially available porous silica support.

Our catalyst allows the selective hydrogenation of nitroarenes under mild conditions while tolerating various functional groups and hydrogenation-sensitive examples such as iodine, nitrile or olefinic groups. The use of the nickel salen complex as metal precursor is crucial for the high activity and selectivity observed.

Introduction

The selective hydrogenation of functionalized aromatic nitro compounds towards the corresponding aniline derivates using heterogeneous catalysts and hydrogen gas as a reducing agent has been investigated intensively in recent years.[1–6] The resulting products are important educts or intermediates for the industrial production of fine chemicals, pharmaceuticals, agrochemicals, polymers, or dyes.[1–6,7] Therefore it is very important that the catalysts, to be developed, are able to tolerate hydrogenation sensitive functional groups such as nitriles, halogenides, ketones, aldehydes or C–C double or triple bonds. The selective hydrogenation of halogen-substituted nitroarenes is particularly an important step for industrial applications as the resulting products can be further functional-ized, for example by cross-coupling reactions.[1,8] The nano-structured gold catalyst (Au/TiO$_2$) reported by Corma and Serna in 2006 was a milestone in the development of new catalysts for the selective hydrogenation of nitroarenes as the catalyst showed remarkably high selectivity patterns.[9] Great efforts have been made since then to develop new heterogeneous catalysts especially using earth-abundant metals instead of noble metals. Such catalysts offer several advantages such as lower prices, resource conservation and eventually novel selectivity patterns.[1] Through the years, the performance of such catalysts has been steadily improved, resulting in an improvement of reaction conditions (pressure, temperature, catalyst loading) but also in an improvement of selectivity patterns. Excellent cobalt[10] and nickel[11–14] catalysts were synthesized in particular. Remarkably low catalyst loadings could be achieved with respect to nickel catalysts using the Ni/C catalyst published by Zhang and coworkers[11] or the montmorillonite supported Nickel catalyst from Dutta and Dutta.[12] No general applicability was demonstrated, although the catalyst loadings were quite low. For the Ni/C catalyst, additional high temperatures had to be applied.[11,12] Two further excellent nickel catalysts were introduced by the Beller group[13] (intermetallic nickel silicide nanocatalyst) and Advani and coworkers[14] (nickel on N-doped carbon nanotubes) respectively. The high selectivity of the catalysts is demon-strated by a broad substrate scope. Mild conditions could be applied for both catalysts. In case of the nickel silicide nanocatalyst, a wide application in various hydrogenation reactions was shown using the catalyst for the hydrogenation of aldehydes, ketones, nitriles, imines, alkenes, alkynes and quinolines.[13] We reported an early example of a nanostructured and selective nickel nitroarene hydrogenation catalyst[15] and recently, our group introduced a new synthesis route for 3,4-dihydro-2H-pyroles from ketones, aldehydes and nitro alkanes via hydrogenative cyclization.[16] The key to this novel reaction was a Ni/SiO$_2$ catalyst capable of hydrogenating aliphatic nitro compounds and tolerating ketones.[16] These results motivated us to investigate the nitroarene hydrogenation capability of our Ni/SiO$_2$ catalyst. Herein, we report on the ability of a reusable and nanostructured nickel catalyst for the hydrogenation of functionalized nitroarenes. The catalyst is synthesized from a nickel salen complex and a commercially available porous silica support. It permits the selective hydrogenation of nitroarenes under mild conditions while tolerating various functional

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groups and hydrogenation-sensitive examples such as iodine, nitrile or olefinic groups.

Results and Discussion

For the synthesis of the Ni/SiO$_2$ catalyst, a well-established and simple synthesis concept, introduced by our group, was used, employing metal salen complexes as precursors and commercially available support materials.[16–20] At first, the SiO$_2$ support material is wet impregnated with a solution of the nickel salen complex (Ni—sal) in acetonitrile, followed by a pyrolysis (700 °C, N$_2$) and a reduction step (500 °C, N$_2$/H$_2$; Figure 1). This catalyst has already been fully characterized.[16] Decomposition of the salen complex during synthesis results in the formation of nickel nanoparticles with a small diameter of 4.7 nm and an N-doped carbon shell around the particles.[16] Such N-doped carbon shells were also found earlier for nickel catalysts synthesized according to this concept.[17,18] It is also assumed that the sublimation behavior of the salen complexes leads to an atomic dispersion of the complex prior to decomposition.[19] Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis revealed a metal loading of 2.8 wt% Ni in the material (Table S1), while X-ray photoelectron spectroscopy (XPS) analysis (Figure S1) indicated two nickel species: metallic Ni^0 and Ni^{2+}. Air handling could partly oxidize the surface of the metallic nanoparticles and surface oxidized metallic Ni-NPs could be formed.[16]
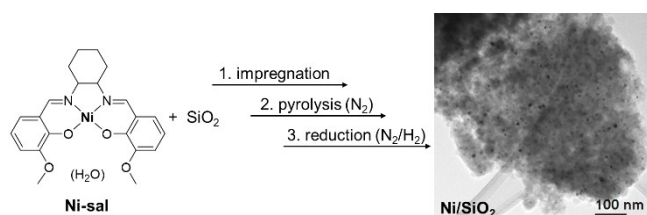

Figure 1. Catalyst synthesis. 1. Wet impregnation of the SiO$_2$ support material with a solution of the nickel salen complex (Ni—sal) in acetonitrile. 2. Pyrolysis of the material at 700 °C in a constant nitrogen stream. 3. Reduction of the pyrolyzed material in a constant stream of forming gas (N$_2$/H$_2$; 90/10).

We choose the hydrogenation of 1-chloro-4-nitrobenzene to 4-chloroaniline as a benchmark reaction for the optimization of the reaction conditions (Table 1). A solvent screening reveals methylcyclohexane as the best solvent for the hydrogenation (Table S1). By increasing the reaction temperature from 20 °C to 40 °C (Table 1, entry 1–3), a quantitative yield of the desired product can be obtained. Decreasing of the H$_2$ pressure did not lead to any further improvement (Table 1, entry 4). The optimized reaction conditions are therefore 0.8 mol% Ni, 40 °C and 10 bar H$_2$. It should be noted that with the use of only 0.8 mol% Ni a really small amount of nickel is necessary to achieve very good yields; moreover, mild reaction conditions can be applied.

We conclude that the use of the nickel salen complex is crucial for the high activity of the catalyst. Therefore, we synthesized five other SiO$_2$-based catalysts for comparison using different commercially available Ni salts as metal sources. Only the use of nickel(II)-acetylacetonate (Ni(acac)$_2$) or nickel(II)-acetate (Ni(OAc)$_2$) as precursor resulted in an observable activity. Compared to our Ni/SiO$_2$ catalyst, however, the yields were quite low (Table 2, entry 1–2, 4). When the other precursor salts nickel(II)-stearate, nickel(II)-nitrate (Ni(NO$_3$)$_2$) and nickel(II)-chloride (NiCl$_2$) were used, no conversion of 1-chloro-4-nitrobenzene was detected (Table 2, entry 3, 5–6), demonstrating the superiority of using the nickel salen complex as metal source. In addition, the nickel loading of the catalyst also plays a decisive role, because when less nickel is used for the synthesis of the material, significant lower yields were detected (Table 2, entry 7–8). If more nickel is employed, the resulting catalyst also shows good catalytic activity in the screening reaction (Table 2, entry 9) but compared to the catalyst with 2.8 wt% nickel loading the yields were lower (Table 2, entry 1).

In order to determine the selectivity of our catalyst, especially the tolerance of functional groups, we investigated its scope. In the hydrogenation of nitrobenzene to aniline, a yield of more than 99% (Figure 2, **1**) was obtained at 40 °C. For

Table 1. Optimization of the reaction conditions.[a]

Entry	Temperature [°C]	Pressure [bar]	Yield [%]
1	20	10	27
2	30	10	67
3	40	10	>99
4	40	5	75

[a] Reaction conditions:0.5 mmol 1-chloro-4-nitrobenzene, 0.8 mol% Ni (2.8 wt% Ni, 0.004 mmol Ni, 0.22 mg Ni), 3 mL methylcyclohexane, 20 h; yields were determined by GC using n-dodecane as an internal standard.

Table 2. Catalyst Screening.[a]

Entry	Metal source	Yield [%]
1	Ni—sal	>99
2	Ni(acac)$_2$	19
3	Ni(II)-stearate	0
4	Ni(OAc)$_2$·4 H$_2$O	8
5	Ni(NO$_3$)$_2$·6 H$_2$O	0
6	NiCl$_2$·6 H$_2$O	0
7 [b]	Ni—sal	27
8 [c]	Ni—sal	18
9 [d]	Ni—sal	85

[a] Reaction conditions:0.5 mmol 1-chloro-4-nitrobenzene, 0.8 mol% Ni (2.8 wt% Ni, 0.004 mmol Ni, 0.22 mg Ni), 40 °C, 10 bar H$_2$, 3 mL methylcyclohexane, 20 h; [b], [c] and [d] nickel catalysts with different Ni wt% loadings. [b] 0.8 mol% Ni (1 wt% Ni); [c] 0.8 mol% Ni (2 wt% Ni); [d] 0.8 mol% Ni (4 wt% Ni); yields were determined by GC using n-dodecane as an internal standard.
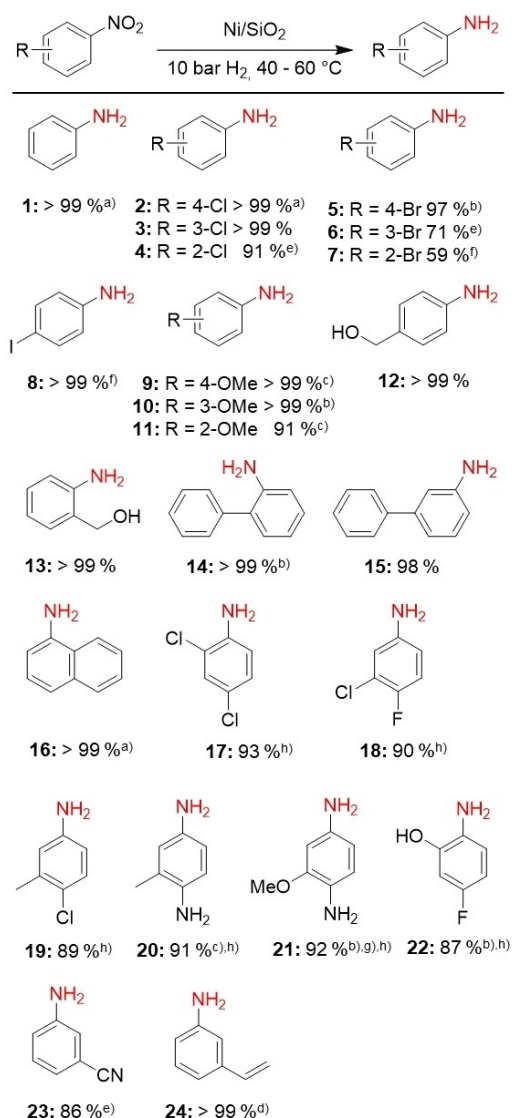
Figure 2. Chemoselective hydrogenation of substituted nitroarenes using Ni/SiO₂. Reaction conditions: 0.5 mmol substrate, 0.8 mol% Ni (2.8 wt% Ni, 0.004 mmol Ni, 0.22 mg Ni), 50 °C, 10 bar H₂, 3 mL methylcyclohexane, 20 h; yields were determined by GC using n-dodecane as an internal standard and identified by GC coupled with a mass spectrometer (GC-MS); a) 40 °C; b) 60 °C; c) 1.2 mol% Ni (2.8 wt% Ni, 0.006 mmol Ni, 0.33 mg Ni), 60 °C; d) 1.5 mol% Ni (2.8 wt% Ni, 0.0075 mmol Ni, 0.41 mg Ni), 60 °C; e) 1.6 mol% Ni (2.8 wt% Ni, 0.008 mmol Ni, 0.44 mg Ni), 60 °C; f) 2.4 mol% Ni (2.8 wt% Ni, 0.012 mmol Ni, 0.66 mg Ni), 60 °C; g) H₂O as solvent; h) isolated yield of the corresponding hydrochloride salt.

the other nitrobenzene derivates, it was necessary to increase the temperature of the catalysis or the Ni content to achieve good yields and high selectivity. Substrates with electron-withdrawing groups, such as *ortho-*, *meta-* and *para*-halogenated nitroarenes (R = −Cl, −Br, Figure 2, **2–7**), were converted into the corresponding aniline derivatives firstly. Even a nitroarene bearing iodine as a substitute (Figure 2, **8**) could be reduced in a good yield of 81%. More electron donating groups, such as methoxy in *ortho-*, *meta-* and *para*-position, or a

−CH₂−OH group in *ortho-* or *meta*-position showed no effect on the catalytic activity of the Ni/SiO₂ catalyst and resulted in excellent yields of 99% (Figure 2, **9–13**) or 91% for the 1-methoxy-2-nitrobenzene, respectively (Figure 2, **11**). Diaryl substrates (Figure 2, **14–16**) could also be hydrogenated up to very good yields of 80%–99% by adjusting the reaction conditions. We investigated substrates containing two substituents next. The introduction of two electron withdrawing halogens in different ring positions resulted in yields of 93% (Figure 2, **17**) and 90% (Figure 2, **18**) of the desired amine. Furthermore, the combination of a methyl substituent with a further chlorine (Figure 2, **19**) did not affect the activity of the catalyst and lead to a yield of 89%. For a nitrobenzene derivate with a methyl and an amino function, the amount of nickel (1.2 mol%) as well as the reaction temperature (60 °C) had to be increased achieving a yield of 91% (Figure 2, **20**). The reaction temperature during the catalysis should also be 60 °C for the two following substrates. The nitroarenes carrying a methoxy and an amino group (Figure 2, **21**) or a fluorine and an alcohol group (Figure 2, **22**) as substituents were converted into the corresponding amines in good yields of 92% and 87%. For compound **21**, water had to be used as a solvent. Finally, we studied two nitroarenes bearing hydrogenation-sensitive functional groups. We first investigated the hydrogenation of 3-nitrobenzonitrile (Figure 2, **23**). The corresponding product, 3-aminobenzonitrile, was acquired without any side product with a yield of 86%. The selective hydrogenation of 3-nitrostyrene to 3-vinylaniline (Figure 2, **24**) was possible to our delight with a yield of 99% by adjusting the catalyst loading to 1.5 mol% Ni without hydrogenation of the double bond. Selective hydrogenation of this challenging substrate has already been investigated using different nanostrucutred heterogeneous 3d-metal catalysts.[21]

To investigate the recyclability of the Ni/SiO₂ catalyst for this reaction, the hydrogenation of nitrobenzene was studied using 0.8 mol% of nickel, 10 bar H₂, 40 °C and 16 h reaction time (Figure 3). Around 80% yield of aniline were obtained under these conditions and no loss of activity was observed after five runs. After a reaction time of two hours the initial rate of reaction was also calculated for each run (Figure 3), again showing no significant loss of activity overall. After the recycle study, the reused catalyst was analyzed by ICP-OES and transmission electron microscopy (TEM). The ICP-OES analysis revealed a metal loading of still 2.75 wt% Ni (Table S1), while TEM analysis (Figure S2) revealed homogeneously distributed nanoparticles with a slightly increased diameter of 5.5 nm compared to the "fresh" catalyst.

Conclusions

In conclusion, we introduced a nickel catalyst for the selective hydrogenation of nitroarenes under mild reaction conditions. 24 differently substituted nitroarenes were hydrogenated to the corresponding amine derivates. Our catalyst showed a high functional group tolerance towards hydrogenation-sensitive functional groups such as iodine, nitrile or a double bond.
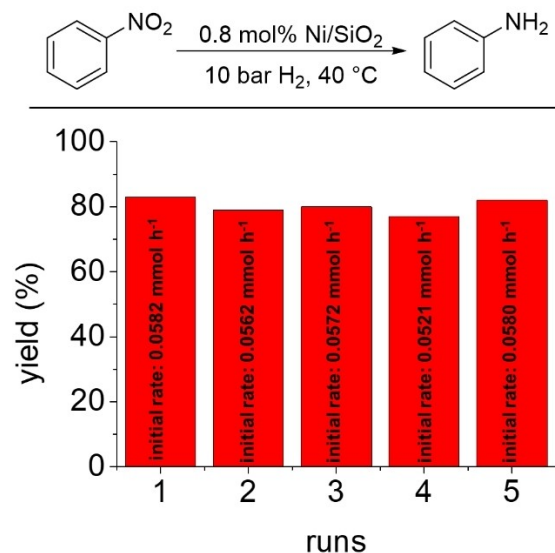
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Figure 3. Reusability of the Ni/SiO$_2$ catalyst using the hydrogenation of nitrobenzene including initial rates. Reaction conditions: 0,5 mmol nitrobenzene, 0.8 mol% Ni (2.8 wt% Ni, 0.004 mmol Ni, 0.22 mg Ni), 40 °C, 10 bar H$_2$, 3 mL methylcyclohexane, 16 h. Conditions for the initial rate: 2 h instead of 16 h; yields were determined by GC using n-dodecane as an internal standard.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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