Selective Hydrogenation of Fatty Nitriles to Primary Fatty Amines: Catalyst Evaluation and Optimization Starting from Octanenitrile

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In this contribution, an evaluation of the potential of various homogeneous and heterogeneous catalysts for a selective hydrogenation of fatty nitriles toward primary amines is reported exemplified for the conversion of octanenitrile into octane-1-amine as a model reaction. When using heterogeneous catalysts such as the ruthenium catalyst Ru/C, the palladium catalyst Pd/C, and the platinum catalyst Pt/Al$_2$O$_3$, low selectivities in the hydrogenation are observed, thus leading to a large portion of secondary and tertiary amine side-products. For example, when using Ru/C as a heterogeneous catalyst, high conversions of up to 99% are obtained but the selectivity remains low with a percentage of the primary amine being at 60% at the highest. The study further reveals a high potential of homogeneous ruthenium and manganese catalysts. When also taking into account economical considerations with respect to the metal price, in particular, manganese catalysts turn out to be attractive for the desired transformation and their application in the model reaction leads to the desired primary amine product with excellent conversion, selectivity, and high yield.

Practical Applications: This work describes an optimized hydrogenation process for transforming fatty nitriles to their corresponding primary amines. In general, fatty amines belong to the most applied fatty acid-derived compounds in the chemical industry with an annual product volume exceeding 800 000 tons per year in 2011 and are widely required in the chemical industry since such compounds are either directly used in home products such as fabric softeners, dishwashing liquids, car wash detergents, or carpet cleaners or in a broad range of industrial products, for example, lubricating additives, flotation agents, dispersants, emulsifiers, corrosion inhibitors, fungicides, and bactericides, showing additional major applications, e.g., in the detergents industry. Among them primary amines play an important industrial role. However, a major concern of current processes is the lack of selectivity and the formation of secondary and tertiary amines as side-products. By modifying a recently developed catalytic system based on manganese as economically attractive and environmentally benign metal component an efficient and selective access to fatty amines when starting from the corresponding nitriles is achieved. For example, hydrogenation of octanenitrile leads to a synthesis of octane-1-amine with >99% conversion and excellent selectivity with formation of secondary and tertiary amine side-products being suppressed to an amount of <1%.
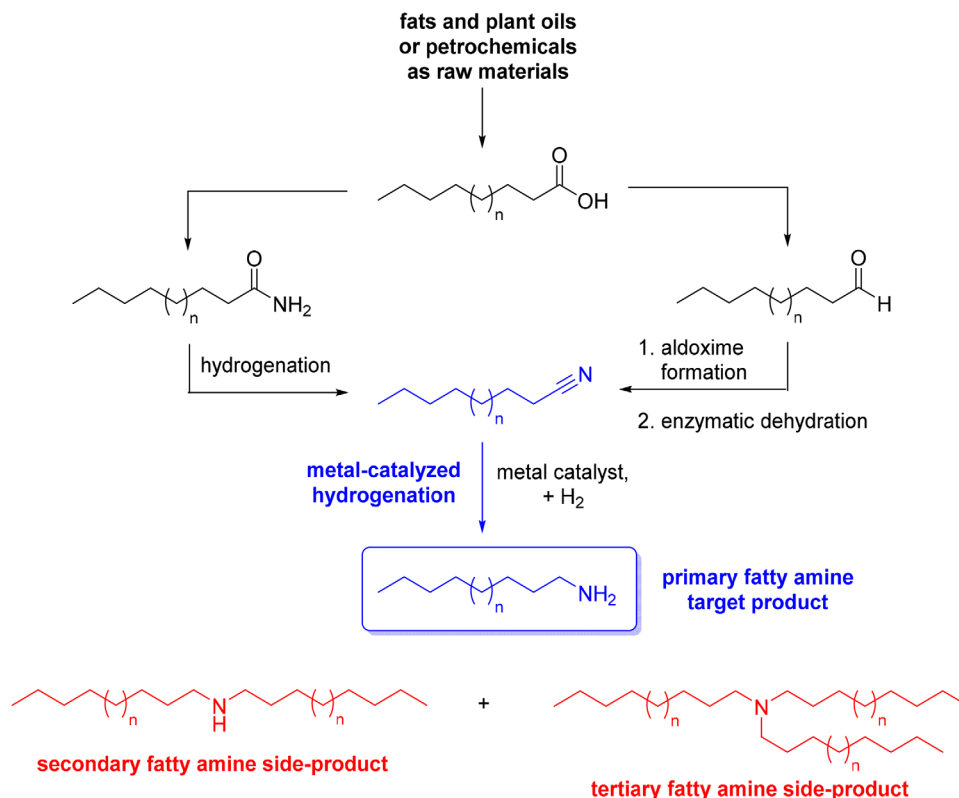
1. Introduction

Fatty amines play an important role in the chemical industry since such compounds are either directly used in home products such as fabric softeners, dishwashing liquids, car wash detergents, or carpet cleaners or in a broad range of industrial products, for example, lubricating additives, flotation agents, dispersants, emulsifiers, corrosion inhibitors, fungicides, and bactericides.[1–3] The worldwide demand of fatty amines was

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800 000 tons in 2011,[3] thus representing a further large-scale option for the use of fats and oils as renewable building blocks and alternative raw material sources to petrochemicals. Among them, primary fatty amine are highly requested target products. When starting from fats and oils, today's established large-scale applied route is based on the hydrogenation of fatty nitriles (**Scheme 1**).

Such fatty nitriles needed as substrates are today industrially manufactured via transformation of vegetable oils through their acids into fatty amides, followed by subsequent dehydration into their corresponding fatty nitriles under high temperatures of 280–360 °C and frequently in the presence of a metal oxide catalyst (Scheme 1).[1] As an alternative to this route via the amide intermediate (which shows disadvantages such as the required high reaction temperatures),[1] such fatty nitriles can be also prepared by a chemoenzymatic pathway starting from fatty aldehydes as further type of fatty acid derivatives (Scheme 1),[4–6]

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Scheme 1. Overview about the overall industrial production concept for primary fatty amines.

Recently, we demonstrated such a process being suitable to be operated at high substrate loading of up to 1.4 kg L⁻¹ aqueous medium exemplified for octanenitrile.[5]

However, in spite of straightforward accesses to the fatty nitrile substrates and established hydrogenation technologies at large industrial scale, a hurdle that remained widely unsolved up to now in this field of fatty amines is the insufficient selectivity of the hydrogenation process (Scheme 1). Typically, with the currently applied heterogeneous metal catalysts the corresponding secondary and tertiary amines are also formed besides the desired primary amine products. For example, when using Pd/C as a heterogeneous catalyst (being frequently used for various types of hydrogenation reactions), the tertiary amine is formed as a major product in the hydrogenation of aliphatic nitriles.[7,8] Also in case of the heterogeneous catalysts Ru/C[9] and Raney nickel,[10,11] insufficient selectivities toward the primary amine have been observed. Although some modifications of hydrogenation conditions and additives were found, which positively influence the selectivity of the Ni-catalyst for primary amines in the hydrogenation of nitriles, there is still a demand for general procedures to hydrogenate various nitriles and in particular aliphatic nitriles selectively to primary amines.[12,13]
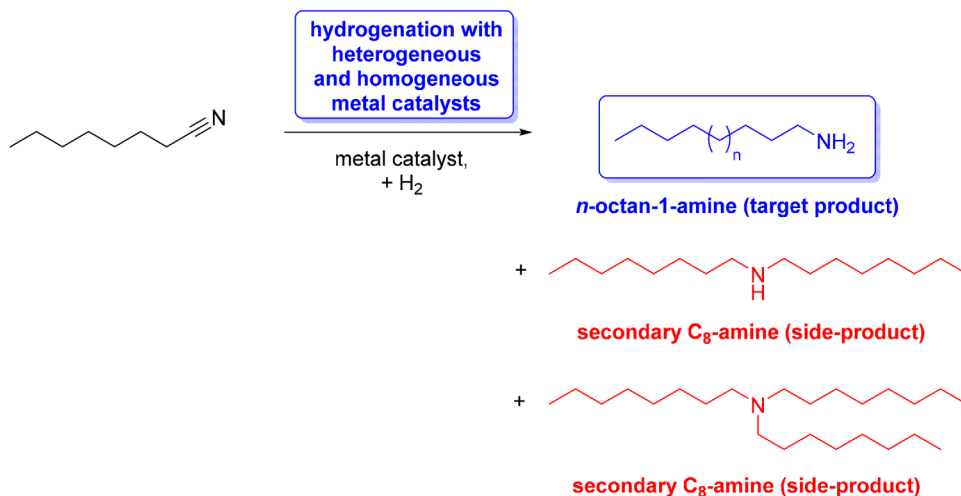
A perspective to overcome these hurdles can be seen in the use of homogeneous in spite of the today's applied heterogeneous catalysts. Due to the option to vary the ligand sphere, selectivity can be fine-tuned, thus shifting the selectivity into direction of the desired primary amines. However, again there are some challenges to solve: often homogeneous catalysts for this purpose

are based on expensive heavy metals. Further issues to be solved are the tasks of high catalytic efficiently (and, thus, high turnover number) and bulk technically feasible strategies for separating and reusing the catalysts. Addressing the first two issues of using a low cost metal component being ideally environmental benign and achieving a high efficiency besides excellent selectivity, we became interested to explore manganese catalysts. Our interest in such catalysts was sparked by the recent achievements from the Kirchner group[14,15] who reported on hydrogenation of various nitriles using such manganese catalysts.

In the following, we report our results on the search of a suitable catalyst providing both high efficiency as well as selectivity for the hydrogenation of fatty nitriles exemplified for octanenitrile (**Scheme 2**). This study comprised an initial re-evaluation of various types of heterogeneous and homogeneous metal catalysts in terms of selectivity and a subsequent study and optimization of a manganese hydrogenation catalysts, which turned out to be promising for the desired reaction.

2. Results and Discussion

First, we defined a model reaction for our catalyst evaluation study and chose the hydrogenation of octanenitrile into octan-1-amine as representative reaction due to practical and analytical reasons. After having established a NMR-based -analytical method for the determination of the reaction course, we started with the screening of a range of heterogeneous catalysts as such

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Scheme 2. Hydrogenation of octanenitrile as model reaction.

Table 1. Hydrogenation of octanenitrile (**1**) using the heterogeneous ruthenium catalyst Ru/C.
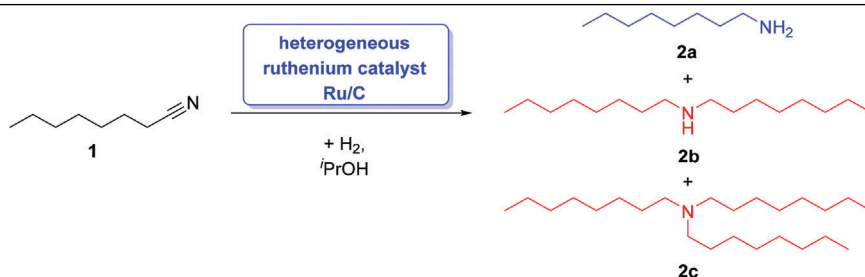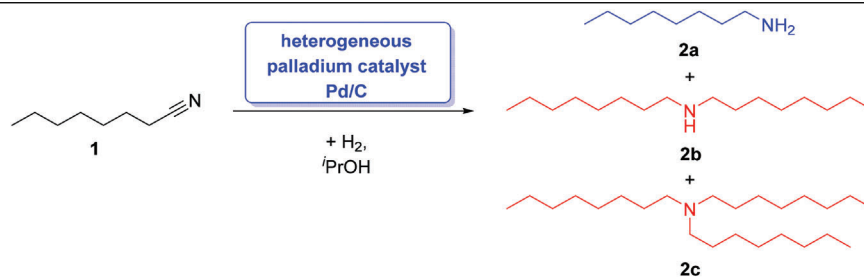

Catalyst	T [°C]	p [bar]	t [h]	Conversion [%]	2a/2b/2c
Ru/C (1 mol%)	27	14	20	–	n.d.
Ru/C (1 mol%)	27	22	20	–	n.d.
Ru/C (5 mol%)	27	13	20	–	n.d.
Ru/C (5 mol%)	27	22	20	–	n.d.
Ru/C (1 mol%)	27	1	19	–	n.d.
Ru/C (5 mol%)	27	1	19	–	n.d.
Ru/C (1 mol%)	100	10	20	72	45/53/2
Ru/C (1 mol%)	100	20	20	77	50/48/2
Ru/C (5 mol%)	100	10	20	71	45/54/1
Ru/C (5 mol%)	100	20	20	81	45/52/3
Ru/C (1 mol%)	80	1	19	–	n.d.
Ru/C (5 mol%)	80	1	19	–	n.d.
Ru/C (1 mol%)[a]	100	20	20	99	60/37/3

[a] Addition of 2 equivalents NH_3 to the hydrogenation reaction.

types of catalysts are today used in industry, thus representing the industrial benchmark. Furthermore, we were interested whether adjusting the reaction conditions to mild conditions would in principle enable a sufficient reactivity while achieving an improvement in terms of selectivity. To start with the heterogeneous ruthenium catalyst Ru/C,[9,16] we varied the temperature broadly between 27 and 100 °C in addition to the hydrogen pressure, which was adjusted between 1 and 22 bar (**Table 1**). The reaction time remains relatively constant at 19 or 20 h, respectively. It turned out that in general an elevated temperature of 100 °C is needed for this transformation, reaching conversions of 71% to 99% in these cases. For the latter case, addition of ammonia (2 equivalents) was needed. In general, ammonia is added to hydrogenation reactions of nitriles in order to prevent the formation of secondary and tertiary amines,[9] since ammonia then serves as an alternative to the amine in the reaction with

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Table 2. Hydrogenation of octanenitrile (**1**) using the heterogeneous palladium catalyst Pd/C.

Catalyst	T [°C]	p [bar]	t [h]	Conversion [%]	2a/2b/2c
Pd/C (10 mol%)	25	1	21	>99	0/96/4
Pd/C (10 mol%)[a]	25	10	21	>99	5/77/18
Pd/C (10 mol%)	25	10	21	>99	0/81/19
Pd/C (10 mol%)	25	20	21	>99	0/89/11
Pd/C (10 mol%)[a]	25	20	21	>99	5/82/13
Pd/C (1 mol%)	25	10	21	88	0/53/47
Pd/C (0.1 mol%)	25	10	21	65	0/65/35
Pd/C (0.05 mol%)	25	10	21	27	11/70/19
Pd/C (1 mol%)	25	1	21	>99	0/62/38
Pd/C (0.1 mol%)	25	1	21	<1	n.d.
Pd/C (1 mol%)[a]	25	20	20	>99	4/45/51

[a] Addition of 2 equivalents NH_3 to the hydrogenation reaction.

the imine intermediate. An elevated hydrogen pressure (20 bar in comparison to 10 bar) had a slightly positive impact on the conversion of nitriles, although the selectivity with respect to the formation of primary, secondary, or tertiary amines is not significantly influenced (Table 1). However, it is noteworthy that independent of the reaction conditions (and even when adding ammonia as a strategy to suppress formation of secondary and tertiary amines), the selectivity remained low with a percentage of the desired primary amine being at 60% at the highest. Thus, formation of secondary and tertiary amines remained as severe side-reactions having a significant impact in general when using Ru/C as a heterogeneous catalyst.

The formation of such side products are a result of the derivatization of the formed primary amine products, which are converted into imines and subsequently reduced to secondary amines.[16] An analogous derivatization of the secondary amine then gives the tertiary amine.

A further heterogeneous catalyst being commonly used for metal-catalyzed hydrogenation is Pd/C.[7,8,16–18] When operating under smooth reaction conditions such as 25 °C as reaction temperature and 1–20 bar hydrogen pressure, a minimum amount of 1 mol% of the catalyst Pd/C was found to be needed for achieving a high conversion within a reaction time of 20 or 21 h (**Table 2**). For example, >99% conversion was obtained at just 1 bar of hydrogen pressure and at a low reaction temperature of 25 °C. However, the amount of the desired primary fatty amine was very low with 0–4% under such conditions. Even when varying the catalyst loading between 0.05 and 10 mol%, the highest percentage of the primary amine product compared to the secondary and tertiary amine products was only 11%

(Table 2). Varying the hydrogen pressure and catalyst loading does not have a strong impact on the selectivity of the hydrogenation reaction. When using this catalyst, the major product was always found to be the secondary amine even when ammonia was added as an additive (the only exception is the reaction with 1 mol% Pd/C and 20 bar of hydrogen, which gave the tertiary amine as major product). However, as expected, the conversion of the nitrile drops with the decrease of the catalyst loading.

Besides ruthenium and palladium, platinum is a further metal component being frequently used for hydrogenation purpose.[19–21] When utilizing Pt/Al_2O_3 as a catalyst at a catalytic loading of 1 mol%, a high conversion of up to 92% was achieved when operating at a hydrogen pressure of 20 bar and at a reaction temperature of 100 °C (**Table 3**). However, again the selectivity was limited and the percentage of the desired primary amine did not exceed 44%. In contrast to the hydrogenation experiments with the Ru/C catalyst, we could not find any or only a very low positive effect of the addition of ammonia on the selectivity of the hydrogenation when using Pd/C or Pt/Al_2O_3 as a catalyst. While in case of Ru/C, the product ratio changed from 45/52/3 to 60/37/3, which shows that a significantly larger amount of primary amine was formed during the reaction in the presence of added ammonia, in case of Pt/Al_2O_3, the ratio did not improve in terms of formation of the primary amine, and in case of Pd/C only a slightly increased amount of primary amine was formed.

In general, these results are in accordance to those in literature for the hydrogenation of nitriles to amines in the presence of heterogeneous catalysts.[7–13] For example, Sajiki et al. showed

Table 3. Hydrogenation of octanenitrile (**1**) using the heterogeneous platinum catalyst Pt/Al$_2$O$_3$.
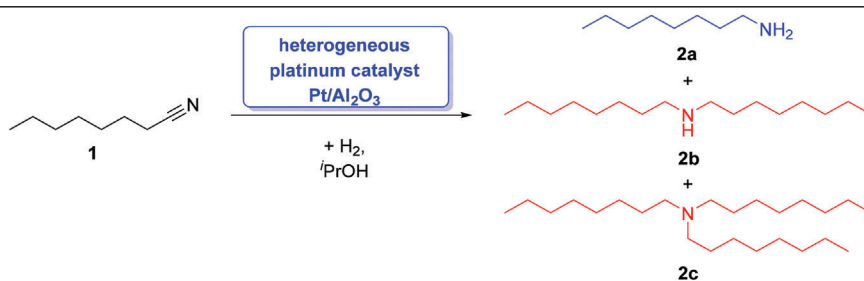
Catalyst	T [°C]	p [bar]	t [h]	Conversion [%]	2a/2b/2c
Pt/Al$_2$O$_3$ 1 mol%)	100	20	20	85	44/53/3
Pt/Al$_2$O$_3$ 1 mol%)[a]	100	20	20	92	41/56/3

[a] Addition of 2 equivalents NH$_3$ to the hydrogenation reaction.

that utilizing Pd/C as heterogeneous catalyst at 25°C and H$_2$ atmosphere for the hydrogenation of decanenitrile in methanol mainly leads to the secondary and tertiary amine.[7] This result is in principle in good agreement with our findings when using this catalyst in isopropanol for the hydrogenation of octanenitrile (Table 2). In our case, at atmospheric pressure of hydrogen at room temperature mainly the secondary amine was formed as a product. Compared to our study in literature often other nitrile substrates were used such as 3-methoxy propionitrile,[9] benzonitrile,[18] decanenitrile,[7] or pentanenitrile,[8] which makes a direct comparison of conversions, yields, and selectivities difficult. However, in particular in case of pentanenitrile[7] and decanenitrile,[8] which are structurally close to our model substrate octanenitrile, the results in literature[7,8] and from our study appear to be comparable.

Taking into account the low selectivities and high amount of unfavored side-products when using heterogeneous catalysts, we turned our interest to the evaluation of homogeneous catalysts for the model reaction. Homogeneous catalysis in our cases always means that the catalyst is dissolved in the reaction mixture during the hydrogenation reaction. Furthermore, even after the hydrogenation reaction the reaction mixture was found to homogeneous without precipitation of catalyst or additives. Based on the work of Beller et al. with ruthenium catalysts,[22] we applied various species for the hydrogenation of octanenitrile in different solvents (**Table 4**). The best results were obtained when using the commercial Ru-MACHO-BH catalyst [23] in isopropanol or alternatively the Ru-Gusev catalyst,[24,25] which turned to be suitable in various solvents such as isopropanol, diisopropylethyer, and cyclohexane. In these hydrogenations, high conversions in the range of 81–99% were obtained at a catalyst loading of 0.5 mol%. Furthermore, excellent selectivities were achieved in such hydrogenations with an amount of desired product of at least 98%. For example, when using the Takasago catalyst Ru-MACHO-BH,[18] 98% conversion and a product ratio of >99:0:0 were observed in our model reaction.

The increased selectivity of hydrogenation reactions for primary amines when using a homogeneous catalyst in comparison to heterogeneous catalysts might be rationalized by the option of homogeneous catalysis to fine-tune the catalytic complex by means of ligands, which, among other effects, then could result in a different catalytic activity for hydrogenating the various conceivable imine intermediates as precursors for the primary, secondary, and tertiary amine products. In this connection, it should be added that a detailed calculation for the heterogeneous Pd-catalyzed hydrogenation of acetonitrile and the reaction steps toward the corresponding primary, secondary, and tertiary amines have been performed and discussed by Adamczyk.[26]

Next, we focused on the impact of catalyst loading which appears to be even more crucial in homogeneous catalysis due to the more difficult catalyst recovery and re-use compared to heterogeneous catalysis. However, when reducing the catalyst loading to 0.1 mol%, conversion drops significantly and did not exceed 18% (Table 4). Thus, improving catalyst activity as well as stability and developing options for its re-use are a task for future research in this field. At the same time we were seeking for a more economical alternative with respect to the metal component due to the high price of ruthenium being currently in the range of 8.150 \$ kg^{-1}.[27] An economically attractive alternative would be iron or manganese as center ion in homogeneous metal catalysts. Inspired by a successful manganese catalyst reported recently from the Kirchner group[14,15] for being suitable in hydrogenation of various functional groups including nitriles (leading to 93% yield for octanenitrile),[15] we focused on this type of catalysts also for our model reaction. Under slightly different reaction conditions and catalyst structure to those described in literature with a prolonged reaction time from 18 to 19 h and using ethyl instead of *n*-propyl substituents at the phosphine ligand of the manganese complex for practical reasons, we achieved a high conversion of >99% in the presence of 2 mol% of the manganese catalyst **6** (**Table 5**). The reaction was conducted at 100 °C in toluene at a substrate concentration of 144 mм and a hydrogen pressure of 50 bar. After work-up, we obtained octan-1-amine in 68% yield, indicating a loss of product during downstream-processing. In order to further improve stability of this catalyst, we speculated if more rigid derivatives bearing cyclohexyl instead of ethyl substituents also could represent active catalysts with potential for higher stability. Thus, we prepared the new catalyst **7** and to our delight this catalyst led to both, excellent conversion of >99% and yield of 96%.

Table 4. Hydrogenation of octanenitrile (**1**) using the homogeneous ruthenium catalysts 3–5.
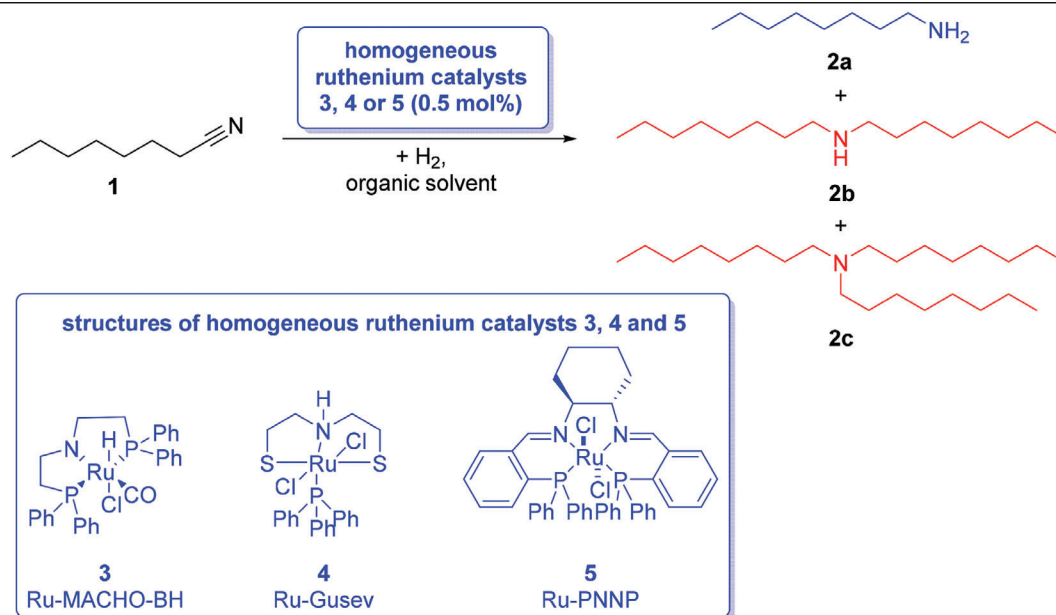
Catalyst	Solvent	T [°C]	p [bar]	t [h]	Conversion [%]	2a/2b/2c
3	^{i}PrOH	70	20	3	98	>99/0/0
3[a]	^{i}PrOH	70	20	3	18	>99/0/0
3	THF	70	20	3	12	>99/0/0
3	^{i}Pr$_2$O	70	20	3	6	86/8/6
3	Cyclohexane	70	20	3	2	>99/0/0
4	^{i}PrOH	70	50	3	99	98/2/2
4	THF	70	50	3	71	65/31/4
4	^{i}Pr$_2$O	70	50	3	98	1/97/2
4	Cyclohexane	70	50	3	81	99/0/1
5	^{i}PrOH	70	60	3	6	0/83/17
5	^{i}Pr$_2$O	70	60	3	9	0/75/25
5	Cyclohexane	70	60	3	<1	0/0/100

[a] In this experiment, 0.1 mol% catalyst loading was used instead of 0.5 mol% (which was the catalyst loading in case of all other experiments shown in Table 4)

Encouraged by these results, we further investigated the hydrogenation of octanenitrile using the Mn^I-catalyst **7** focusing on reduction of the catalyst loading as a next step (**Table 6**). When reducing the catalyst loading from 2 mol%, which was used in the initial experiment, to 1, 0.5, and 0.1 mol%, we could obtain a quantitative conversion towards octane-1-amine without identifying secondary or tertiary amines as by-product in case of 1 mol%. By lowering the catalyst loading to 0.5 mol%, however, a decreased conversion of 51% toward the primary amine was found.
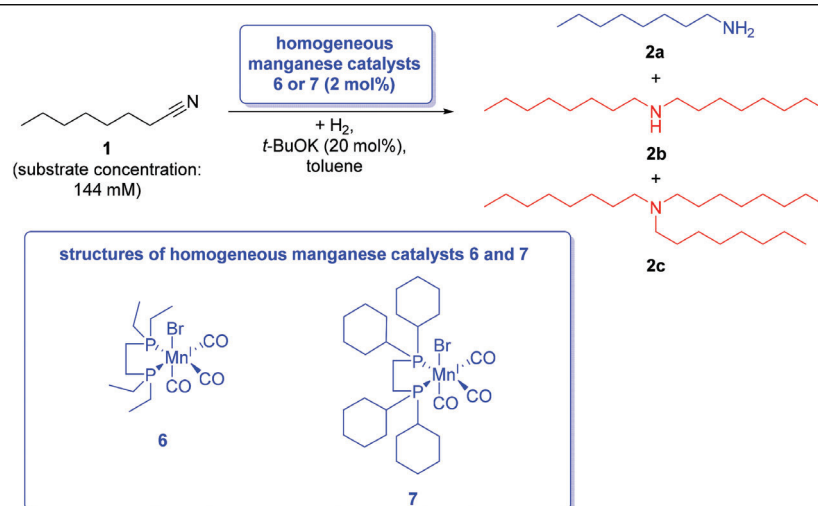
In addition, we investigated the impact of different solvents on this hydrogenation reaction. Besides toluene as solvent used in the initial experiments with the Mn-catalysts **6** and **7**, we tested tetrahydrofurane (THF), 2-methyl tetrahydrofurane (2-Me-THF), ethanol, and isopropanol (Table 6). When using a catalyst loading of 2 mol% of catalyst **7**, full conversion toward the primary amine was reached in all cases without formation of by-products. However, at a decreased catalyst loading of 1 mol% of catalyst **7**, only in case of toluene and 2-Me-THF a full conversion was obtained, while the use of ethanol, isopropanol, and THF led to lower conversions.

After optimization of the hydrogenation conditions for the synthesis of octane-1-amine, we conducted a hydrogenation experiment under such optimized conditions using dodecanenitrile (**8**) as a substrate (**Scheme 3**).

When using this fatty nitrile **8** as a starting material and the manganese complex **7** as a catalyst at a catalytic loading of 1 mol%, also full conversion to the primary amine **9a** without formation of secondary or tertiary amines was obtained. This experiment indicates that this hydrogenation method is applicable for the synthesis of various fatty primary amines of different chain-lengths starting from the corresponding aliphatic nitriles.

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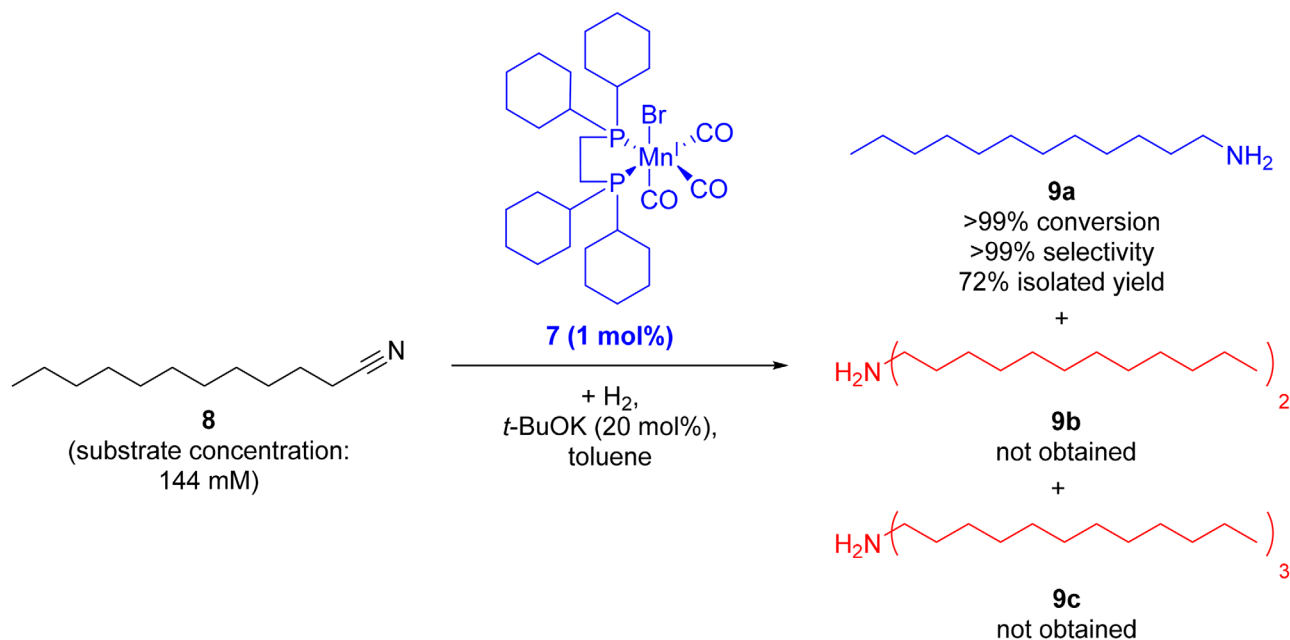**Table 5.** Hydrogenation of octanenitrile (**1**) using the homogeneous manganese catalysts **6** and **7**.

Catalyst	T [°C]	p [bar]	t [h]	Conversion [%]	Yield [%]	2a/2b/2c
6	100	50	19	>99	68	>99/0/0
7	100	50	19	>99	96	>99/0/0

Table 6. Hydrogenation of *n*-octanenitrile (**1**) using the homogeneous manganese catalyst **7**—optimization experiments in terms of catalyst loading and solvent.
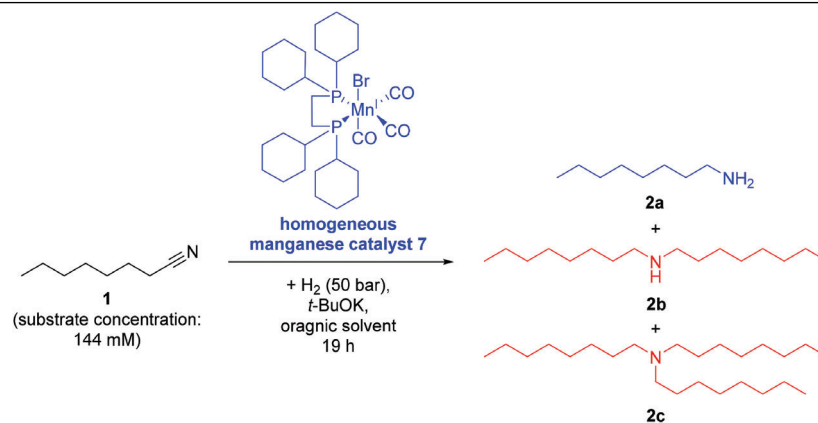
Catalyst loading	*t*-BuOK loading	Organic solvent	T [°C]	Conversion [%]	2a/2b/2c
2 mol%[a]	20 mol%	Toluene	100	>99	>99/0/0
1 mol%	10 mol%	Toluene	100	>99	>99/0/0
0.5 mol%	5 mol%	Toluene	100	51	51/0/0
0.1 mol%	1 mol%	Toluene	100	<1	n.d.
2 mol%	20 mol%	THF	100	>99	>99/0/0
2 mol%	20 mol%	2-Me-THF	100	>99	>99/0/0
2 mol%	20 mol%	Ethanol	100	>99	>99/0/0
2 mol%	20 mol%	Isopropanol	100	>99	>99/0/0
1 mol%	10 mol%	THF	100	71	>99/0/0
1 mol%	10 mol%	2-Me-THF	100	>99	>99/0/0
1 mol%	10 mol%	Ethanol	100	53	>99/0/0
1 mol%	10 mol%	Isopropanol	100	58	>99/0/0

[a] This experiment is also shown in Table 5.

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Scheme 3. Hydrogenation of dodecanenitrile using Mn-catalyst **7**.

3. Conclusions

In conclusion, an evaluation of the potential of various homogeneous and heterogeneous catalysts for a selective hydrogenation of fatty nitriles toward primary amines was done exemplified for the conversion of octanenitrile into octan-1-amine as a model reaction. When using heterogeneous catalysts, low selectivities were observed, thus leading to a large portion of secondary and tertiary amine side-products. The study further revealed a high potential of homogeneous ruthenium and manganese catalysts. When also taking into account economical considerations with respect to the metal price, in particular manganese catalysts turned out to be attractive for the desired transformation and their application in the model reaction led to the desired primary amine product with excellent conversion and selectivity and in high yield.

4. Experimental Section

Hydrogenation reactions were performed in a Parr Series 5000 Multiple Reactor System in which up to six different hydrogenations were conducted in parallel. The maximum volume of the used autoclaves was 75 mL and the reaction mixtures were stirred at 1000 rpm. In case of heterogeneous catalysts, a Teflon inlet was used to prevent adsorption of the catalyst to the stainless-steel autoclave material. Before usage of the reactors, they were evaporated and filled with Argon twice. Afterward the nitrile (250 mM in all cases except for hydrogenations using Mn^I-catalysts **6** and **7**) and solvent (10 mL total volume) were added in an Argon counter flow. Finally, the catalyst and potentially used additives were added under inert conditions. In case of heterogeneous catalysts sometimes ammonia was used as an additive. Ammonia (2 eq based on nitrile concentration) was added by adding ammonia in methanol (7 M) to the reaction mixture. Manganese catalysts **6** and **7** were used in combination with t-BuOK (10x catalyst concentration, e.g. 10 mol% t-BuOK when 1 mol% **6** or **7** was used) as additive. The autoclaves were placed into the Parr Series

5000 Multiple Reactor System, which among others consists of a burst protection for high pressure reactions. The reactors were washed with nitrogen (3 × ≈20 bar) to prevent formation of oxyhydrogen gas formation and afterward with hydrogen (2 × ≈20 bar, 1× required pressure) before adjusting the hydrogen-pressure to required pressure in every reactor. After stirring for the desired reaction time, the autoclaves were washed with nitrogen (3 × ≈20 bar) before cooling to room temperature and work-up. Heterogeneous catalysts were filtered and homogeneous catalysts were removed by filtration over a ≈2 cm celite (Celite 545, Merck) layer. The filter cake or celite layer was washed with solvent (same as used in hydrogenation experiment) twice (each ≈5 mL). The solvent was removed in vacuo and the product was analyzed by ^{1}H-NMR spectroscopy and ESI–MS. NMR spectra were recorded on a Bruker Avance III 500 at a frequency of 500 MHz (^{1}H) or 125 MHz (^{13}C). Chemical shift δ was given in ppm and referenced to the corresponding solvent signal (CDCl$_3$). Nano-ESI mass spectra were recorded using an Esquire 3000 ion trap mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a nano-ESI source. Samples were dissolved in methanol or acetonitrile and introduced by static nano-ESI using in-house pulled glass emitters. Nitrogen served both as nebulizer gas and dry gas. Nitrogen was generated by a Bruker nitrogen generator NGM 11. Helium served as cooling gas for the ion trap and collision gas for MS^n experiments. The mass axis was externally calibrated with ESI-L Tuning Mix (Agilent Technologies, Santa Clara, CA, USA) as calibration standard.

Octan-1-amine (**2a**): ^{1}H-NMR (500 MHz, CDCl$_3$) δ/ppm = 2.66 (t, 2H, NH$_2$-CH_2-(CH$_2$)$_6$-CH$_3$), 1.42-1.29 (m, 12H, NH$_2$-CH$_2$-(CH_2)$_6$-CH$_3$), 0.86 (t, 3H, -CH_3).

ESI-MS (positive ions) [C$_8$H$_{19}$N+H]$^+$ m/z (calc.) = 130.15, m/z (exp.) = 130.10.

Dodecan-1-amine (**9a**): ^{1}H-NMR (500 MHz, CDCl$_3$) δ/ppm = 2.69 (t, 2H, NH$_2$-CH_2-(CH$_2$)$_6$-CH$_3$), 1.43-1.25 (m, 20H, NH$_2$-CH$_2$-(CH_2)$_6$-CH$_3$), 0.87 (t, 3H, -CH_3).

ESI-MS (positive ions) [C$_{12}$H$_{27}$N+H]$^+$ m/z (calc.) = 186.21, m/z (exp.) = 186.12.

Abbreviation

equiv, equivalents

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Supporting Information

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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