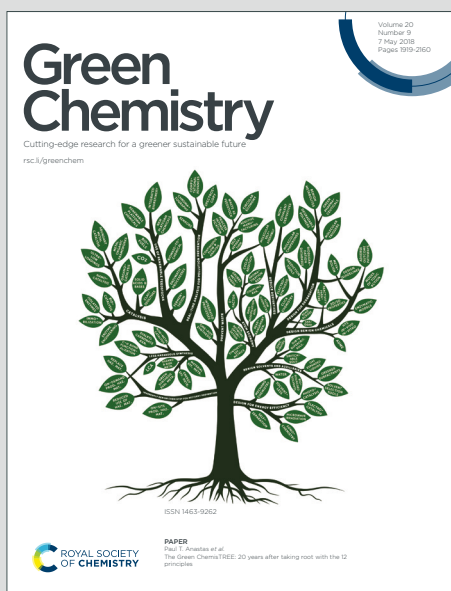


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One-pot reductive amination of carboxylic acids: a sustainable method for primary amine synthesis

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The reductive amination of carboxylic acids is a very green, efficient and sustainable method for the production of (bio-based) amines. However, with current technology, this reaction requires two to three reaction steps. Here, we report the first (heterogeneous) catalytic system for the one-pot reductive amination of carboxylic acids to amines, with solely H₂ and NH₃ as the reactants. This reaction can be performed with relatively cheap ruthenium-tungsten bimetallic catalysts in the green and benign solvent cyclopentyl methyl ether (CPME). Selectivities of up to 99% for the primary amine could be achieved at high conversions. Additionally, the catalyst is recyclable and tolerant for common impurities such as water and cations (e.g. sodium carboxylate).

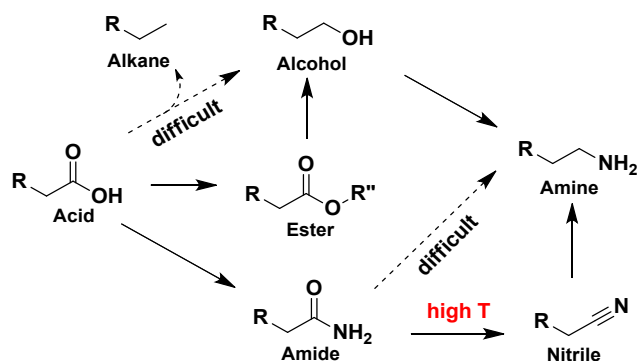
Introduction

Amines are important compounds in the chemical and pharmaceutical industry. With an annual production of more than 6 million ton/year, they are widely used for the production of agrochemicals, pharmaceutical ingredients, dyes, polymers, fabric softeners, detergents, solvents, lubricants etc.¹⁻³ Historically, reductive amination of carbonyl compounds is one of the most popular methods for amine synthesis.^{1,4} While in the past the starting compounds were often oil-based, progress has been made in recent years in producing amines from bio-based compounds like alcohols, ketones, aldehydes and amino acids.⁵⁻¹⁷ While these methods are very successful, reductive amination of carboxylic acids could be a desirable complementary method for sustainable amine synthesis.

Carboxylic acids are generally cheap and readily available, e.g. from fermentation¹⁸ or from hydrocarbon oxidation; many fatty acids can be gained from biomass or from industrial waste streams¹⁹. This makes them suitable platform chemicals. For the production of several bio-based amines, carboxylic acids are already the main starting material, e.g. fatty acids for fatty amines, or sebacic acid for 1,10-diaminodecane, which allows synthesis of high-value polyamides. Additionally, in a biorefinery, the production of carboxylic acids is generally more efficient than the fermentative production of the corresponding aldehydes or alcohols.²⁰⁻²¹

Currently, carboxylic acids can be converted to the corresponding primary amine via one of two possible pathways (Figure 1). The first pathway runs through the corresponding alcohol (upper pathway Figure 1). Since the catalytic reduction of carboxylic acids is more difficult than ester hydrogenations, the molecule is esterified first²²⁻²³. Next, the ester is reduced after which, in a third reaction step, a classic amination occurs. In order to shorten this pathway to a two-step procedure, one can immediately reduce the carboxylic acid to the alcohol. Over the years, many reduction catalysts have been described for this reaction. However, these catalysts are expensive, since most of them are based on a platinum group metal (PGM) or/and Re, and easily overreduce the carboxylic acid towards unfunctionalized alkanes.²⁴⁻⁴¹ The second pathway involves the formation of an amide, which is dehydrated towards a nitrile at temperatures above 250°C, typically with a ZnO catalyst, and reduced afterwards (lower pathway Figure 1). This is the most common synthesis method for fatty amines.⁴² We recently demonstrated that the direct hydrogenation of primary amides is a very efficient and green method to produce primary amines, reducing this second pathway to a two-step procedure as well.⁴³ Nevertheless, a one-pot synthesis of primary amines from carboxylic acids would be a significant improvement in comparison with the current multi-step pathways, regarding energy cost, reactor cost and product isolation.

Current routes



This work

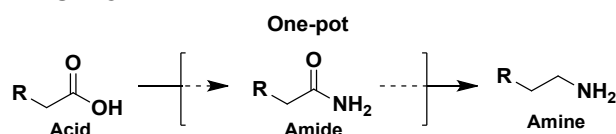


Figure 1 – Synthesis pathways to amines from carboxylic acids.

The direct synthesis of primary amines from carboxylic acids is a fairly unexplored domain, especially using NH_3 and H_2 .^{44-45, 63} To the best of our knowledge, the only report of a (heterogeneous) catalyst for the reductive amination of carboxylic acids, is a CuCrO_2 -catalyst described by Barrault et al.⁶³ Their catalytic system, however, leaves much room for improvement; the substrate scope was limited to dodecanoic acid, relatively severe reaction conditions were required (i.e. 300°C) and only 27% yield of dodecylamine was obtained. For the *N*-alkylation of amines with carboxylic acids, a closely related reaction, several homogeneous catalysts have been described based on Ru, Pt, Ir, B etc. using silanes (resulting in stoichiometric amounts of waste) or H_2 as the reducing agent.⁴⁶⁻⁵³ Especially in the teams of Beller and Cole-Hamilton extensive research was performed, with a Ru-Triphos complex as a commonly used alkylation catalyst.⁴⁹⁻⁵³ Although both teams achieved excellent yields for a variety of products, it appears that the catalyst requires an activated amine, in particular an aromatic amine. The synthesis of primary aliphatic amines with this Ru-Triphos catalyst was not successful, as was demonstrated by Margo et al.: a direct hydrogenation of nonanoic acid in the presence of NH_3 only yielded 15% nonylamine and 47% dinonylamine. Another closely related work was performed by Jamil et al.⁵⁴ They successfully converted triglycerides into amines with a heterogeneous Pt/ ZrO_2 catalyst, bypassing the amide pathway entirely (Figure 1). Although a significant yield of 59% dodecylamine and 32% didodecylamine was achieved, the reaction required an extremely long reaction time of 36 h, with 5 mol% Pt.

In this work, we report recyclable supported RuWO_x -catalysts as highly efficient catalysts for the one-pot reductive amination of a wide variety of carboxylic acids, yielding primary amines (70-96%) and the corresponding secondary amine as the main side product. Reactions were performed in the green and benign cyclopentyl methyl ether (CPME) as solvent, under mild hydrogenation conditions, i.e. with limited addition of NH_3 and H_2 . To our knowledge, this is the first report of an efficient (heterogeneous) reductive amination system for carboxylic acids, yielding primary amines.

Results and discussion

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Unraveling the reaction network

When performing hydrogenation reactions with amides, in the presence of NH_3 , it was noticed that replacing the amide reactant with a carboxylic acid resulted in high yields of the corresponding amine as well.⁴³ Therefore, a time profile was made to look more closely into the reaction network of the octanoic acid (**1**) amination, using a $\text{RuWO}_x/\text{MgAl}_2\text{O}_4$ catalyst at 200°C (Figure 2). It appears that at the onset of the reductive amination, the acid is quite rapidly converted to the amide. Since this catalyst was designed for the reduction of primary amides, a further hydrogenation towards the primary amine proceeded smoothly. However, there are several differences compared to a 'simple' amide hydrogenation. Firstly, whereas the dehydration of the ammonium carboxylate to the amide is very fast at the onset of the reaction, it takes a very long time to fully deplete the carboxylic acid. This is remarkable, since this dehydration in the absence of H_2 is fully completed within two hours (Figure S 2). Thus, it appears that the carboxylic acid forms a rather stable salt with the freshly formed alkylamine, drastically lowering the dehydration rate. Secondly, full defunctionalization and secondary amide formation are two noticeable side reactions. While these side reactions were nearly negligible in amide hydrogenation reactions, here 10% of the initial product was lost at full conversion (yields of 5% *N*-octyloctanamide (**7**), 3% heptane (**6**), 2% octane (**5**); see reaction scheme in Figure 3). These two observations suggest that, although a one-step reaction is possible, it may be more effective to first form the amide in the absence of H_2 , and next pressurize the vessel with H_2 .

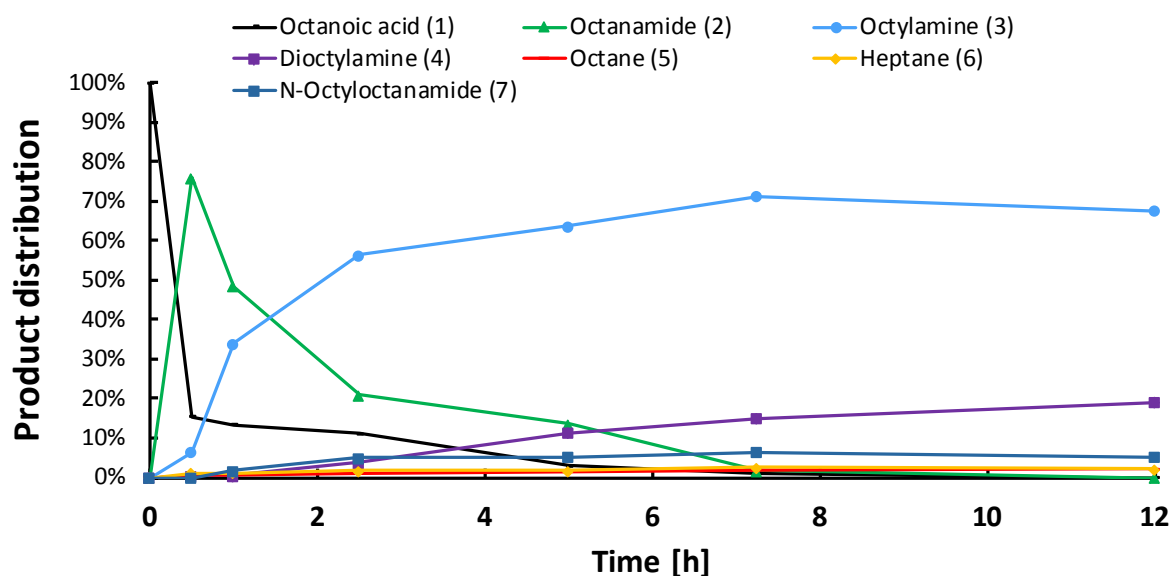


Figure 2 – Time profile for the reductive amination of octanoic acid. Reaction conditions: octanoic acid (1 mmol), 200°C , 6 bar NH_3 , 50 bar H_2 , 5 mol% Ru (4 wt% Ru on $\text{RuWO}_x/\text{MgAl}_2\text{O}_4$), undecane standard (20 μL), CPME (10 mL).

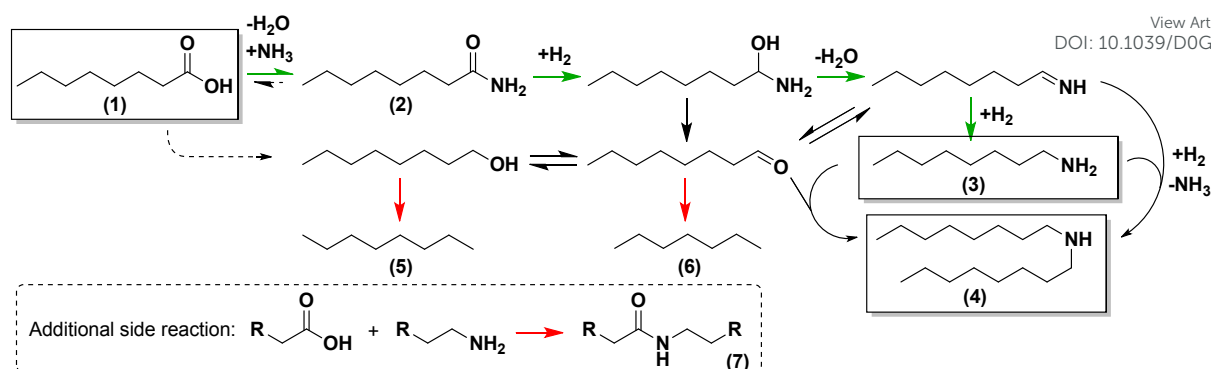


Figure 3 – Reaction network for the catalytic reductive amination of carboxylic acids

Catalyst evaluation

These results raise the question how the primary amide is formed, and whether the dehydration of the ammonium carboxylate is a catalytic or spontaneous reaction. It appears that the catalyst support is essential for the dehydration towards primary amides. Several supports were screened for their dehydration activity (Figure 4). Generally, these experiments suggest that the dehydration could be catalyzed by either basic or acidic sites. On the one hand, the rather basic supports $MgAl_2O_4$ and ZrO_2 yielded 82% and 85% octanamide (2) respectively.^{43,61} On the other hand, the clearly acidic support Nb_2O_5 , featuring both Brønsted and Lewis acid sites yielded 75% of octanamide (2) and was even able to promote the dehydration to the nitrile, resulting in 10% octanenitrile.⁶² TiO_2 performed well as well.⁵⁵⁻⁵⁶ The only slightly acidic SiO_2 and the homogeneous Lewis acid catalyst $Y(OTf)_3$ performed poorly. In the blank reaction, only small amounts of primary amide were formed (4% yield). It should be noted that in the hydrogenation of primary amides with bimetallic catalysts, a basic support is recommended to steer the selectivity to primary amines instead than to secondary amines. When inserting the amide formation as a first step, a basic nature of the support is useful to improve the catalytic activity as well. For $MgAl_2O_4$, ZrO_2 and TiO_2 , CO_2 - and NH_3 -TPD measurements were performed. The measured acidic and basic properties are very similar to those described in literature (Figure S 7 and Table S 1).^{55-56,61}

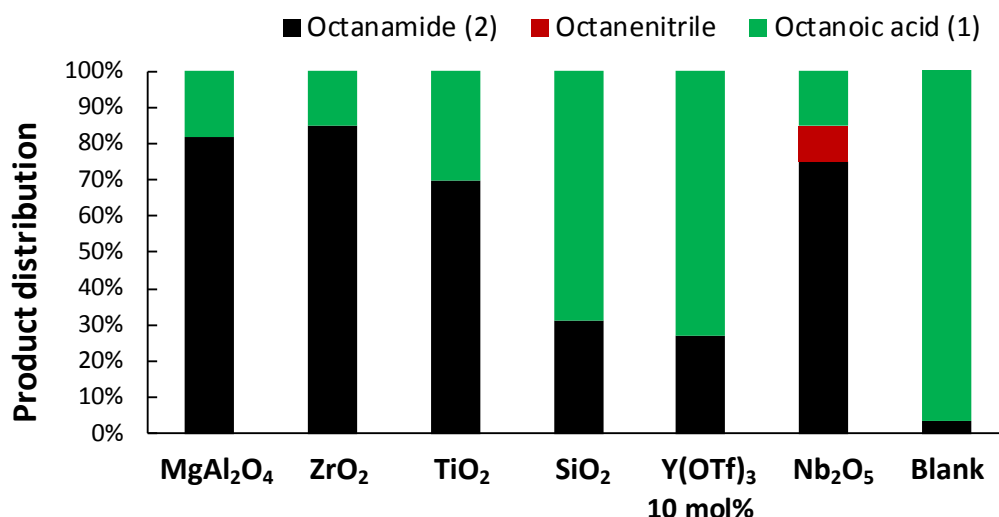


Figure 4 – Dehydration of ammonium carboxylate, formed from octanoic acid and ammonia, in the presence of different supports. Reaction conditions: octanoic acid (1 mmol), 200°C, 6 bar NH_3 , 0.126 g catalyst support, undecane (20 μ L), CPME (10 mL), 1 h.

Next, a catalyst evaluation was performed. In our previous work, RuWO_x-catalysts were proven to be highly efficient for the reduction of aliphatic amides. Such a bimetallic catalyst contains a noble metal and a Lewis acid metal oxide, in order to facilitate the adsorption of the amide to the catalyst's surface. While the catalyst support only mildly affects catalytic activity in the separate amide reaction, it now accomplishes the dehydration of the ammonium carboxylate. It is therefore unclear how RuWO_x-catalysts position themselves (in terms of catalytic activity) compared to commercially available and other highly active amide hydrogenation catalysts. For this reason, several WO_x-modified Ru catalysts were prepared and compared to commercial PGM/C, as well as to the highly active amide reduction catalyst PtV/hydroxyapatite (Figure 5).⁵⁷ The commercial catalysts performed poorly: the carbon supports are not suitable for promoting the dehydration reactions, and up to 36% octanoic acid (**1**) was still present after 7 h of reaction time.⁴³ Additionally, the unpromoted noble metals lack amide hydrogenation activity. Only in the case of Ru/C, a noticeable 34% octylamine (**3**) yield was formed along with 12% of the dead-end product *N*-octyloctanamide (**7**). PtV/hydroxyapatite performed better; the basic support ensured a rapid dehydration of the ammonium octanoate, while the promoted Pt provides a considerable hydrogenation activity.⁵⁷⁻⁵⁸ The catalyst, however, lacks selectivity for the primary amine; a lot of *n*-octanol is formed, along with *N*-octyloctanamide (**7**) and octane (**5**) (selectivities of respectively 20%, 7% and 6%). The RuWO_x-catalysts are by far superior. RuWO_x/TiO₂ and RuWO_x/ZrO₂ behave very similarly; yields of 74% and 72% octylamine (**3**), and 11% and 14% dioctylamine (**4**) were obtained respectively. RuWO_x/MgAl₂O₄ is, due to its superior hydrogenation activity, the most active catalyst, leading to a full conversion.⁴³ However, as a result of the consecutive condensation reaction (primary to secondary amines), the *n*-octylamine (**3**) yield is slightly lower, i.e. 70% octylamine (**3**) and 20% dioctylamine (**4**). This small drop can be prevented by shortening the reaction time or adding less catalyst to the reaction mixture; yields of 76% octylamine (**3**) and 8% dioctylamine (**4**) were obtained after a reaction with 6.5 mol% Ru instead of 7.5 mol% (5 h under H₂).

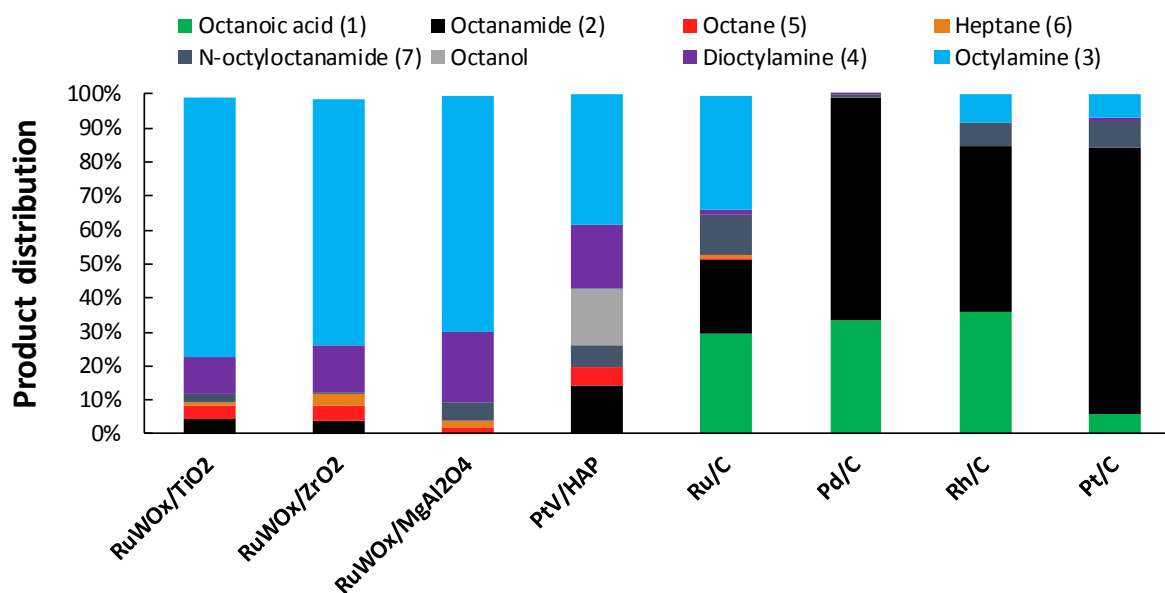


Figure 5 – Catalyst evaluation for the reductive amination of octanoic acid. Reaction conditions: fed-batch reaction, octanoic acid (1 mmol), 200°C, 6 bar NH₃ (initial 2 h), 6 bar NH₃ + 50 bar H₂ (5 h), 7.5 mol% PGM, undecane (20 μL), CPME (10 mL).

Influence of impurities

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Industrial streams of (bio-based) carboxylic acids never have a purity of 100%. Common impurities are cations, e.g. in the form of sodium salts, or water. Therefore, with the aim of achieving an industrially viable process, the influence of impurities was investigated (Figure 6). In general, the catalyst deals very well with these impurities. Small quantities of sodium, e.g. added as 5 % of sodium octanoate, do not have a large effect on the catalytic activity. However, the presence of a larger quantity of strong base induces the decarboxylation of sodium salts to alkanes, leading to 21% heptane (**6**) yield with 0.2 equivalents NaOH.⁵⁹ A reaction with pure sodium octanoate did not yield any hydrogenation products. The addition of 1 vol% water did not hinder the dehydration of the ammonium octanoate, but decreased the hydrogenation rate significantly (35% yield, 90% selectivity for n-octylamine (**3**) after 4 h). We demonstrated before that solvents with alcohol functional groups preferentially adsorb on the W Lewis acid sites of the catalyst, lowering the amide hydrogenation rate.⁴³ Thus, whereas the catalyst keeps its selectivity, in order to maintain a high activity, it is important to have as little water in the reaction mixture as possible. Since the reaction is performed in CPME, this is a relatively simple task. Water has an extremely low solubility in CPME; as little as 0.35 vol% water would result in phase separation at room temperature. Additionally, Dobson et al. clearly demonstrated that drying zeolites could easily remove any water, even at 200°C, ensuring a rapid amide hydrogenation.⁶⁰ Low quantities of water do not hinder the reaction (Figure 6 and S 3).

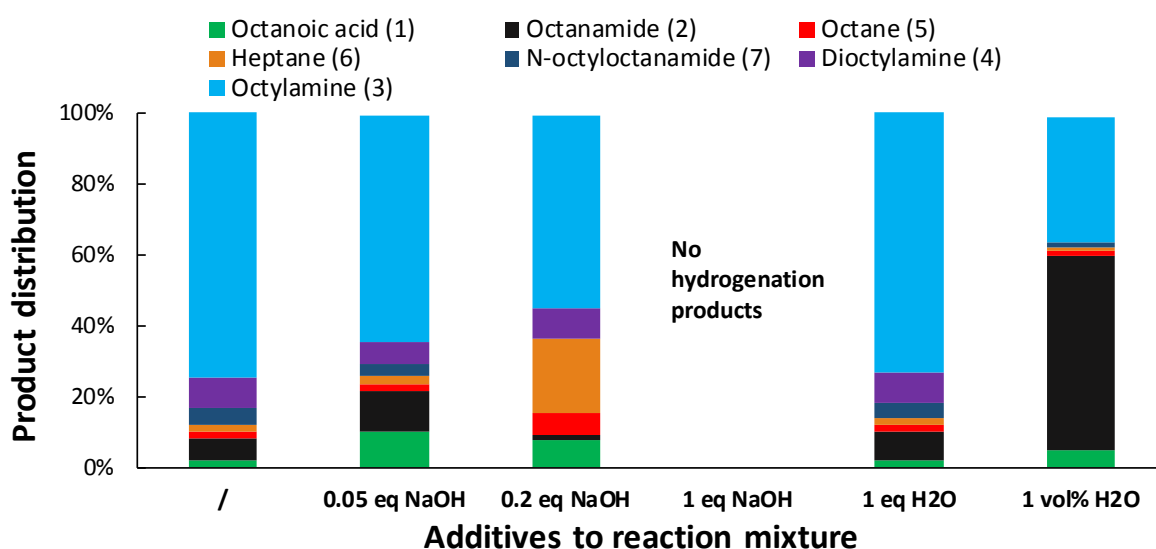


Figure 6 – Influence of sodium and water on the catalytic system. Reaction conditions: batch reaction, octanoic acid (1 mmol), 200°C, 6 bar NH₃, 50 bar H₂, 5 mol% Ru (4 wt% Ru on RuWO_x/MgAl₂O₄), undecane (20 μL), CPME (10 mL), 4 h.

Recyclability of the catalyst

A recycling test was performed to check the stability of the RuWO_x-catalyst. A first series of recycling tests was unsuccessful; after each run with RuWO_x/MgAl₂O₄, there was a significant drop in catalytic activity (Figure S 4). ICP measurements clearly showed that there was a lot of Mg, Ru and W leaching. Since no leaching was observed when performing this recycling test with octanamide (**2**) as the employed substrate and the addition of 1 eq. water (Figure 7), a logical cause is the partial dissolution of the support, caused by the carboxylic acid.^{43,65} As a result, promoted Ru nanoparticles (~2 nm diameter) would float freely in solution, resulting in positive ICP measurements. This hypothesis was proven to be correct; replacing the spinel with insoluble TiO₂ (rutile) or ZrO₂ allowed to maintain the catalytic activity over at least 4 consecutive runs (Figure 8 and Figure S 6).⁶⁶⁻⁶⁷

Thus, for the production of amines from carboxylic acids, we propose a fed-batch set-up in which RuWO_x/TiO₂ or RuWO_x/ZrO₂ is the employed catalyst; after completing a relatively quick dehydration of the ammonium carboxylate (under NH₃ atmosphere), H₂ is fed to the reactor and the hydrogenation is performed. This method bypasses several issues of a batch reaction, such as side reactions and reaction inhibition due to amine formation. Although the employed RuWO_x/TiO₂ or RuWO_x/ZrO₂ catalysts are slightly less active than RuWO_x/MgAl₂O₄, they can perfectly withstand the carboxylic acid's corrosivity.⁶⁶⁻⁶⁷

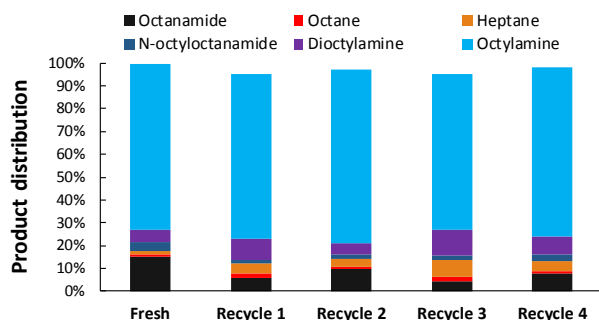


Figure 7 – Recycling of RuWO_x/MgAl₂O₄. Reaction conditions: batch reaction, octanamide (1 mmol), water (1 eq.) 200°C, 6 bar NH₃, 50 bar H₂, 5 mol% Ru, undecane (20 μL), CPME (10 mL), 4 h.

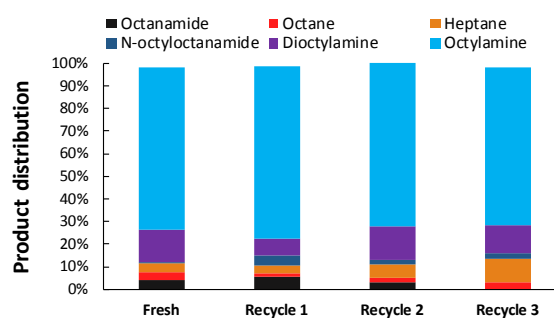
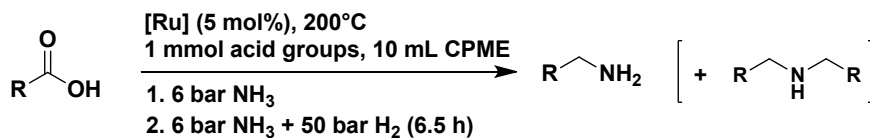


Figure 8 – Recycling of RuWO_x/TiO₂. Reaction conditions: fed-batch reaction, octanoic acid (1 mmol), 200°C, 6 bar NH₃ (initial 2 h), 6 bar NH₃ + 50 bar H₂ (5 h), 7.5 mol% Ru, undecane (20 μL), CPME (10 mL).

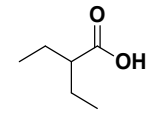
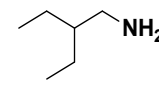
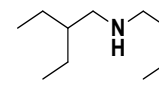
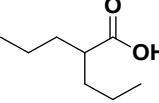
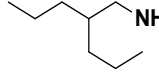
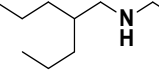
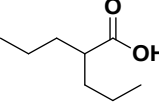
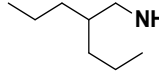
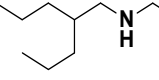
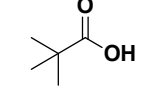
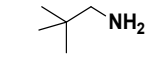
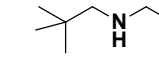
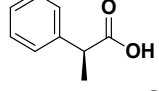
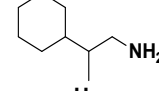
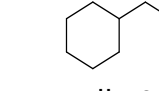
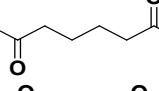
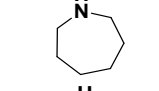
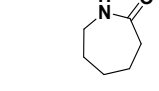
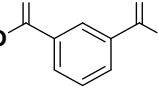
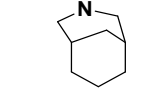
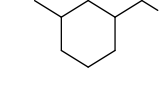
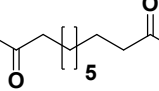
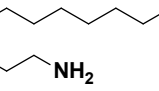
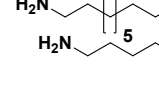
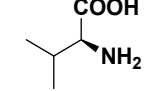
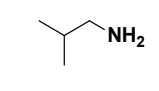
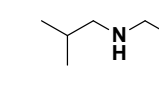
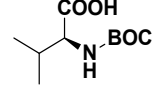
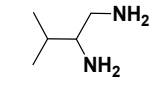
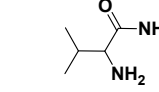
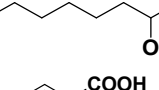
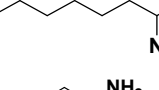
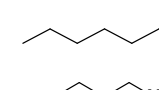
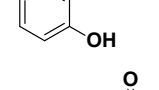
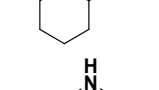
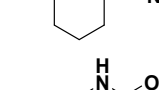
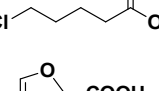
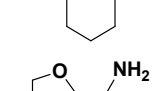
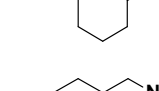
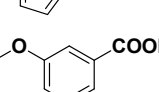
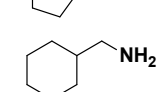
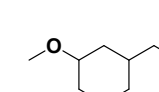
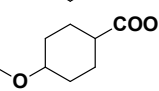
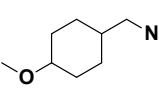
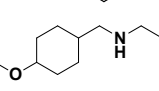
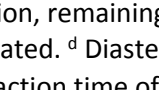
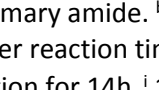
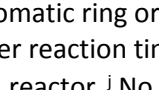
Substrate scope investigation

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Finally, a substrate scope investigation was performed to illustrate the range of applicability (Table 1 & Table S 2). High yields of the corresponding primary amines were obtained for all linear monofunctional carboxylic acids (entries 1–7). These high yields and selectivities (70–85% at nearly full conversion) are consistently obtained for carboxylic acids with chain lengths between C4 and C14. As one might expect, the more reactive corresponding ester of such an acid is rapidly converted towards the amine as well (entry 4). Any unsaturated C-C bonds, like in alkenes and aromatic rings are also readily reduced, as can be expected for a Ru catalyst (entries 5, 9, 10, 19, 21, 26, 28, 29). Preferably, the trans-isomer is formed (entries 10, 21, 29). For branched substrate molecules a clear drop in catalytic activity was observed (entries 8, 11–19). These more bulky molecules are sterically hindered and require a longer reaction time. However, when the aliphatic carboxylic acid is branched at the α -position, the condensation reaction towards secondary amines is nearly completely halted (entries 11–19). This results in extremely high selectivities and yields for the primary amine, with selectivities up to 99%. Even after a reaction time of 5 days with the very bulky 2-propylpentanoic acid (entry 17), only 7% is converted towards the corresponding secondary amine, while the primary amine yield amounts to 82%. Any stereocenters on the α -position, however, will be lost due to the imine-enamine tautomerism. Dicarboxylic acids have the tendency to form cyclic molecules, as was also the case for diamides. Thus, reactions with adipic acid yielded high amounts of azepane and caprolactam (53% and 39% yield respectively; entry 20). Only traces of hexamethylenediamine were formed. Similar results were observed for isophthalic acid, with formation of a bicyclic secondary amine (entry 21). Longer dicarboxylic acids, such as sebacic acid, do not have this tendency towards cyclization. A yield of at least 30% 1,10-diaminodecane was observed. A reaction with an amino acid, i.e. (L)-valine, led mainly to decarboxylation products (entry 23). However, protecting groups on the amine functionality of the amino acid were helpful to obtain the desired diamine (entry 24). As one can expect, based on the proposed reaction scheme (Figure 3), alcohols are easily transformed into amines (entries 25–26). Our catalytic system seems to be extremely selective for the amination of secondary alcohols, resulting in e.g. 98% yield of 2-octylamine from 2-octanol (entry 25). Aliphatic C-Cl bonds are liable to nucleophilic substitution with NH_3 , possibly followed by cyclization to a lactam, or directly with the formed primary amine. A reaction with 5-chlorovaleric acid mainly resulted in the formation of piperidine (85%), with 2-piperidinone (9%) as the main side product. The formation of these products is not surprising; industrially, 11-aminoundecanoic acid (polyamide 11 precursor) is synthesized from 11-bromoundecanoic acid in the presence of NH_3 (spontaneous reaction, even at low temperature $< 90^\circ\text{C}$).⁶⁴ Aromatic C-halogen bonds are degraded upon hydrogenation of the aromatic ring. The major product after an attempted reductive amination of pentafluorobenzoic acid was cyclohexane (55% yield, Table S 2). Finally, the stability of ether bonds was investigated. Ether bonds both located in and (especially) substituted on aromatics rings are somewhat unstable (entries 28–29). However, aliphatic ether bonds are very stable (entry 30).

Table 1 – Substrate scope investigation with RuWO_x-catalyst.View Article Online
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	Substrate	X ^a [%]	Main product	S ^b [%]	Minor product	S ^b [%]
1		95		85		5
2		> 99		76		13
3		95		80		8
4		96		76		12
5		87 ^c		81		8
6		97		76		16
7		> 99		70		20
8		79		76		18
9		96 ^c		81		8
10		99 ^c		81 (57 ^d)		11
11		90		99		< 1
12		> 99 ^e		96		3
13		76		99		< 1
14		47		92		< 1

15		91 ^f		93 ^f		3 ^f	View Article Online DOI:10.1039/D0GC01441A
16		18		96		< 1	
17		94 ^g		88 ^g		8 ^g	
18		74		99		< 1	
19		53 ^h		87		6	
20		> 99 ⁱ		53		39	
21		> 99		57		11 (73 ^d)	
22		> 99		30		55	
23		94		54		5	
24		> 99		20		37	
25 ^j		> 99		98		1	
26		> 99		50		10	
27		> 99		85		9	
28		> 99		43		10	
29		> 99		44		29 (22 ^d)	
30		96		84		8	

^a Conversion, remaining substrate is the primary amide. ^b Selectivity. ^c aromatic ring or alkene is hydrogenated. ^d Diastereomer excess. ^e After reaction time of 16 h. ^f After reaction time of 48 h.

^g After reaction time of 120 h. ^h batch reaction for 14h. ⁱ 1 mmol diacid in reactor. ^j No pre-treatment with NH₃ overnight.

Conclusion

In conclusion, these bimetallic and bifunctional ruthenium – tungsten catalysts perform excellently for the direct reductive amination of carboxylic acids. The employed catalytic system is green, recyclable and relatively cheap. We also demonstrated that the catalyst is tolerant for common impurities (e.g. cations such as Na^+ or water), although it is best to work with as pure as possible reactant streams. Finally, an extensive substrate scope investigation was performed. Good yields and selectivities for the corresponding primary amine were achieved, with values up to 96% and 99% respectively. To our knowledge, this is the first report of a (heterogeneous) reductive amination system for carboxylic acids, yielding primary amines selectively.

Experimental section

Reactions

Reactions were performed in a 25 mL pressure Parr batch reactor. In a typical fed-batch reaction, the reactor is filled with a carboxylic acid (e.g. octanoic acid), RuWO_x -catalyst (5 mol%, 4 wt% Ru, Ru-W ratio of 8-1), undecane (internal standard, 20 μL) and cyclopentyl methyl ether (CPME, 10 mL). Then, the reactor is sealed, purged, pressurized with the desired amounts of NH_3 (typically 6 bar NH_3) and heated to the desired temperature (200°C, stirred at 830 rpm). After the appropriate reaction time the second gas (H_2) was added. For safety reasons, the reactor is first cooled down in an ice bath, after which a desired amount of H_2 is fed to the reactor (50 bar). After a reaction time of 6h30 at 200°C, the reactor is cooled down for the second time in another ice bath. The pressure is then released after which the reactor can be opened. The reaction mixture is transferred to a glass reaction vial (11mL) which is then sealed and centrifuged. The mixture is then analyzed via GC, GC-MS and NMR.

Recycling test

After each reaction, the catalyst was separated from the reaction mixture and washed 2x with ethanol. The catalyst was dried in an oven at 60°C overnight and was reused afterwards. Small quantities of catalyst (1%) that were lost in the process, were replenished with fresh catalyst.

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Conflicts of interest

There are no conflicts to declare.

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