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Is water a suitable solvent for the catalytic amination of alcohols?†

Johannes Niemeier,^a Rebecca V. Engel^{a,b} and Marcus Rose  ^{*a}

The catalytic conversion of biomass and biogenic platform chemicals typically requires the use of solvents. Water is present already in the raw materials and in most cases a suitable solvent for the typically highly polar substrates. Hence, the development of novel catalytic routes for further processing would profit from the optimization of the reaction conditions in the aqueous phase mainly for energetic reasons by avoiding the initial water separation. Herein, we report the amination of biogenic alcohols in aqueous solutions using solid Ru-based catalysts and ammonia as a reactant. The influence of different support materials and bimetallic catalysts is investigated for the amination of isomannide as a biogenic diol. Most importantly, the transferability of the reaction conditions to various other primary and secondary alcohols is successfully proved. Hence, water appears to be a suitable solvent for the sustainable production of biogenic amines and offers great potential for further process development.

Introduction

The catalytic amination of alcohols with ammonia for the production of lower alkyl amines is an industrial process of great importance. Production capacities, e.g., of methyl amines are in the range $>480.000 \text{ t a}^{-1}$ worldwide.¹ The gas phase reaction of methanol and ammonia is carried out at temperatures of 390–430 °C using amorphous silica-alumina catalysts with Lewis- and Brønsted-acidic active sites. Alternatively, more active and shape selective zeolites are used, although they suffer from higher coke formation. Alcohol amination under milder reaction conditions ($T < 200 \text{ °C}$) and based on a different reaction mechanism was developed in the past few decades by applying metal-catalysts with the ability to hydro-genate/de-hydrogenate alcohols.^{2–6} Due to the lower temperatures and the ability to aminate long-chain alcohols, reactions are rather carried out in the liquid phase. Therefore, inert organic solvents are typically used due to a high solubility of most aliphatic alcohols.

With the development of processes for the utilization of renewable resources liquid and especially aqueous phase catalytic conversion is of utmost importance.⁷ In particular, biomass and biomass-derived platform chemicals exhibit a high degree of heteroatom functionalization, mainly in the

form of oxygenate groups.⁸ Hence, biogenic alcohols with an enormous molecular and functional diversity are considered versatile and valuable intermediates for novel chemical value-added chains. Due to the high potential of biogenic amines⁹ in the chemical industry and especially of bifunctional amines for the polymer market,^{10,11} the development of efficient catalytic alcohol amination processes is inevitable as highlighted recently by Pera-Titus and Shi.¹² Based on the higher reactivity of primary and secondary amines compared to ammonia they are quite intensively investigated in the N-alkylation reaction with alcohols. Therefore, various types of molecular and solid catalysts were investigated, e.g., Ir-, Rh-, Ru-complexes,^{13–15} MOF-immobilized Ir-complexes,¹⁶ hydroxyapatite- and polymer-immobilized Ru-species,^{17,18} and even conventional RANEY®.¹⁹ However, especially for bulk amine production the amination of alcohols to primary amines using ammonia as a reactant is of even greater importance. In recent years,

especially molecular Ru-catalysts in organic solutions have been investigated for this purpose.^{15,20–22} It was proved that for these catalysts the amination occurs primarily through the “borrowing hydrogen” concept²³ as proposed earlier.^{24,25} Thereby, the alcohol is de-hydrogenated at the catalytic centre; the ketone reacts with ammonia to the respective imine, which is subsequently re-hydrogenated with the catalyst-bound hydrogen to the final amine. In a few examples the amination of alcohols with ammonia was carried out using solid catalysts. Shimizu et al. reported Ni/Al₂O₃ and Ni/CaSiO₃ and Cui et al. NiCuFeO_x as suitable catalysts for the amination as well as for the N-alkylation reaction of alcohols.^{26–29} However, for these reactions organic solvents were applied, which is less favourable for a large scale amination process of biogenic alcohols.

^aInstitut für Technische und Makromolekulare Chemie, RWTH Aachen University, Worringerweg 2, 52074 Aachen, Germany. E-mail: rose@itmc.rwth-aachen.de

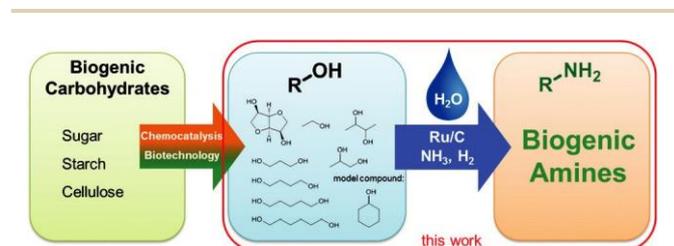
^bCardiff Catalysis Institute, Cardiff University, 42 Park Place, CF10 3AT Cardiff, UK

Takanashi et al. reported, to our knowledge for the first time, the utilization of a Rh–In/C catalyst for the aqueous phase amination of C₃-alcohols.³⁰ However, rather long reaction times of 160 h were required to achieve amine yields of 25%. Recently, we found Ru/C as a much more efficient and recyclable catalyst for the direct amination of biogenic isohexides in aqueous solutions.³¹ Before that, only homogeneous ruthenium catalysts were reported for this transformation.^{21,22}

Isohexides are a class of bifunctional sugar alcohols with a rather rigid bicyclic structure.³² They are derived by a two-fold dehydration of their respective C₆-sugar alcohols and are promising monomers for novel bio-polymers.¹¹ Processing iso-hexides in aqueous solution would be advantageous since they are rather polar molecules that require polar solvents. However, especially for the catalytic amination most polar solvents appear to be too reactive themselves and undergo self-amination. As shown for the homogeneously catalysed amination one of the few suitable solvents is tert-amyl alcohol due to its non-reactive tertiary hydroxyl group.

In the heterogeneously catalysed amination of these compounds the configuration of the starting material directs the product distribution consisting of different mono- and diamines.³¹ Also, a certain hydrogen pressure was required to maintain the catalytic activity although the hydrogen is not consumed. So far, a drawback has been the apparently limited overall yield of diamines, probably due to a reversible product inhibition due to the diamines coordinating strongly to the catalyst surface. Remarkably, the leaching of Ru into the solution under highly basic and hydrothermal conditions was very low. The outstanding performance of Ru as catalysts for carbonyl hydrogenation in the aqueous phase was investigated in the past^{33–38} and recently summarized by Michel and Gallezot.³⁹ Two different explanations are reasonable: (I) co-adsorbed water molecules on the oxophilic Ru surface might lower energy barriers while (II) the dissociation of water results in an increased concentration of hydrogen species on the metal surface.

Since water is a very good solvent for sugar-based platform chemicals and often present in the production of other bio-genic alcohols, the Ru-catalysed aqueous phase amination appears to be a promising approach for further process development towards biogenic amines (Scheme 1). Herein, we investigate in detail the performance and stability of the Ru-based catalysts by varying support materials as well as



Scheme 1 Biogenic carbohydrates can be converted to various alcohols by means of chemocatalysis and biotechnology. This work focuses on the aqueous phase amination of these alcohols using solid Ru-based catalysts.

applying bimetallic catalysts. Most importantly, we prove the transferability of the reaction conditions to various other bio-genic alcohols especially considering the improvement of processing conditions by using water as a green solvent.

Experimental

Catalyst preparation and characterization

Catalysts were prepared by the wet impregnation method. The respective amount of the metal salts was dissolved in 20 mL of ethanol and stirred (750 rpm) for 24 h together with 700 mg of the respective support material. After evaporation of the solvent the materials were dried in air at 120 °C and subsequently reduced in a hydrogen-flow at 350 °C for 4 h. The as-prepared samples were stored under an argon atmosphere until the catalytic experiments. Hydroxyapatite was prepared according to the procedure of Wuyts et al.⁴⁰ Its phase purity was verified by powder diffraction. The ion exchange was performed as described by Peeters et al.¹⁷ The amount of metal on the supports was determined by ICP-OES.

Catalytic amination

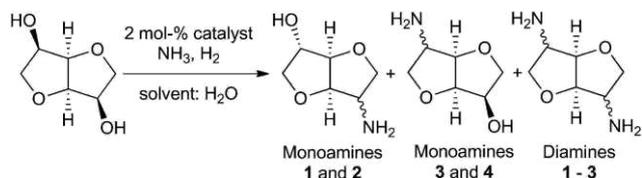
For the amination of isomannide, 1 g (6.84 mmol) of isomannide was stirred (500 rpm) with 2 mol% metal/C (e.g. Ru/C 0.277 g, 0.137 mmol Ru content) in 5 g of an aqueous ammonia solution (25 wt%) in a 45 mL autoclave (Multi Reaction System MRS-5000 from Parr) at 170 °C for 6 h. For screening of the pressure dependence as well as of the various alcohols as substrates 10 mL-autoclaves (Multi Batch System (MBS) from Parr) were used with just one fifth of the charge using 5 wt% Ru/C. Before heating, the autoclave was pressurized with 10 bar of hydrogen at ambient temperature (ca. 20 °C). After the reaction the autoclaves were left to cool down and the solutions were stirred for 1 h under atmospheric conditions to remove the residual ammonia. Thereafter, the catalyst was filtered off. The samples were analyzed via gas chromatography after derivatization according to the recently described procedure.³¹ Metal leaching was determined by direct ICP-OES analysis of the solution.

The catalytic experiments of the different alcohols were performed in principle in the same way as for the isohexide amination. In this case 1.37 mmol of the alcohol was placed together with 2 mol% (with regard to the number of hydroxyl groups) of 5 wt% Ru/C in 1 g of an aqueous ammonia solution (25 wt%) in a 10 mL autoclave pressurized with 10 bar H₂. The solution was stirred (500 rpm) for 6 h at 170 °C. The products were analyzed with quantitative NMR spectroscopy.

Results and discussion

Catalytic amination of isomannide

The product mixture of the aqueous phase amination of isomannide analysed by gas chromatography (GC) contains up to ten different compounds (Scheme 2). Monoamines 1 and 2 occur only as negligible by-products since monoamines can



Scheme 2 The catalytic amination of isomannide results in a mixture of mono- and diamines. Monoamines 1 and 2 are only minor by-products due to the isomerization of the hydroxyl group as a side reaction. The isomers (isosorbide and isoidide) are also observed as side-products.

undergo isomerization of the hydroxyl group configuration due to a de-hydrogenation/re-hydrogenation reaction without the intermediate imine formation step. Thereby, also the thermodynamically favoured isohexide-isomers, isosorbide and isoidide can occur.⁴¹ However, they are found also only in trace amounts since apparently the imine formation is significantly faster than the direct re-hydrogenation of the initially formed ketone. Hence, the major products in the reaction mixtures are monoamines 3 and 4 with the remaining hydroxyl group in endo-configuration as well as the three isomeric di-amines. As found earlier in batch experiments³¹ the total yield of diamines does not exceed 10% while the yield of the mono-amines approaches 40%. Apparently, after initial formation of the diamines they adsorb preferentially on the metal surface, thus, reversibly blocking the active sites for further conversion.

In all batch amination experiments typically the mass balance is not closed by approximately 5–20%. Since especially high surface area support materials such as activated carbon in the Ru/C catalysts are applied, equilibrium adsorption of all compounds in the mixture is very likely. To verify this hypothesis, the spent catalyst was separated from the mixture and washed under reflux conditions for 1 h with chloroform and water, respectively, to further quantify the adsorbed species (Fig. S1†). Thereby it was proved that the incomplete mass balance is majorly based on adsorbed substrates and products. The overall conversion decreases by up to 10% while the total product yield increases by only 2–3% in one washing cycle. This further indicates that more substrate is adsorbed than amination products, a fact that is of interest as a purification step by selective adsorption in the downstream processing.

As mentioned above, a certain hydrogen pressure is required to ensure catalytic activity although it is not stoichiometrically consumed. Following Henry's law the amount of absorbed hydrogen in the aqueous solution depends on the pressure.⁴² Even at higher temperatures and a decreasing solubility of hydrogen, the influence of hydrogen on the amination process is significant. By comparing the dependence of the catalyst activity by batch experiments, two regimes are obvious (Fig. S2†). Up to a pressure of 10 bar at ambient temperature, that corresponds to 25 bar at 170 °C, the catalyst activity apparently linearly depends on the pressure. At least 5 bar at ambient temperature are required to observe a significant formation of amine products. For pressures higher than 10 bar at ambient temperature the selectivity is shifted from the amination

towards the isomerisation products of the isohexides. Apparently, the isomerisation kinetics depends even more on the hydrogen pressure, although, it is not consumed as well.

Influence of the catalyst support

Since water is used as a highly polar solvent for rather polar substrate molecules the use of Ru supported on a porous carbon material is questionable. Activated carbons typically exhibit a rather hydrophobic inner surface. This would be less beneficial for the wettability and hence, the accessibility of the catalytic centres, which is known to be a crucial aspect for a high catalyst efficiency.⁴³ Therefore, we investigated the catalytic performance and stability of different catalyst supports that are able to withstand the harsh hydrothermal and basic reaction conditions. While alumina and silica even partially dissolve under reaction conditions, ceria, titania, zirconia and hydroxyapatite supports appear to be sufficiently stable. The latter was chosen since it was previously applied for the N-alkylation of primary amines with alcohols, although carried out in organic solvents.¹⁷ An outstanding high dispersion is to be expected since the Ru³⁺ ions are introduced by an ion exchange process in the top layers of the hydroxyapatite structures.⁴⁰ All applied catalysts show a conversion of 30–56% (Fig. 1). While titania- and ceria-supported catalysts show a similar activity and selectivity towards the amine products as the Ru/C benchmark catalyst, zirconia- and hydroxyapatite-supported Ru resulted in total amine yields of only 20–25%. All catalysts exhibit the formation of minor amounts of the isomerization products isosorbide and isoidide. Interestingly, the Ru/hydroxyapatite catalyst exclusively results in monoamine 3

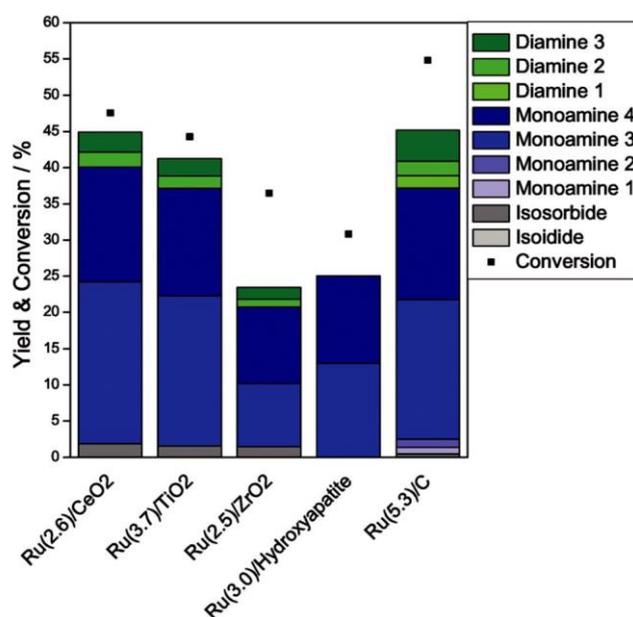


Fig. 1 Comparison of the different support materials for highly dispersed Ru as amination catalysts in aqueous solutions. The values in brackets are the amount of Ru (wt%) on the catalysts as determined by ICP-OES elemental analysis.

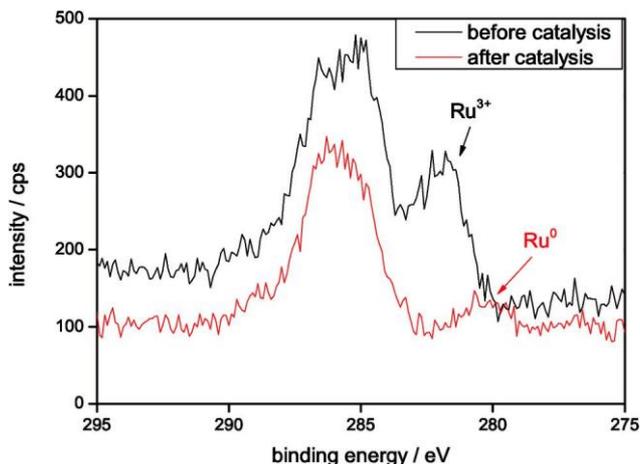


Fig. 2 XPS spectra of Ru/hydroxyapatite before (black) and after (red) catalysis showing the reduction of Ru^{3+} to Ru^0 in the shift of the binding energy from 282 eV to 280 eV.

and 4 as products, while no diamines are formed at all. This high selectivity might be explained by an outstanding high dispersion of the Ru sites, as suggested by Peeters et al.¹⁷ They claimed a stable Ru^{3+} species as catalytically active sites obtained by the ion exchange method. To verify this hypothesis, the catalyst was characterized in greater detail. The hydroxyapatite structure was maintained during the ion exchange to incorporate Ru^{3+} ions as indicated from the powder diffraction pattern (Fig. S3†). Furthermore, before and after catalysis XPS spectra of the Ru/hydroxyapatite material were measured (Fig. 2 and S4†). They clearly confirm that under the applied reductive reaction conditions in an aqueous solution the Ru^{3+} ions are reduced to elemental Ru species. Hence, in aqueous solutions the beneficial effect of highly dispersed Ru^{3+} ions is suppressed since the reduction to elemental Ru^0 nanoparticles dominates.

The catalyst stability under the hydrothermal basic conditions is of utmost importance for further process development. Especially the presence of ammonia and amine products gives rise to the assumption that in solution the formation of metal amine complexes might result in significant leaching. To investigate the stability the metal leaching was determined by ICP-OES quantification of the Ru concentration of the reaction mixture. For all tested supports the concentrations found were below 2 ppm. Apparently, all tested catalysts are equally suitable regarding the stability of the active Ru nanoparticles. Also, no significant differences between the inorganic supports and the activated carbon-support can be observed.

Bimetallic Ru-based catalysts

As shown above, the aqueous phase amination in batch experimentation appears to be limited in the overall yield of amines. Despite the fact that an excess of ammonia is used for all experiments and since especially the diamine yields do not exceed 10%, a limitation of the catalyst activity by coordination of the diamines seems to be likely. Although this product inhi-

tion is reversible by washing the catalyst and re-using it, optimizing the catalysts to achieve higher diamine yields in one batch would be beneficial. In particular, the required down-stream processing either in batch or later on in continuous operation could benefit from higher yields since the process efficiency decreases with an increasing share of reaction mixture that has to be recycled in the reactor after product separation.

Regarding the strong diamine coordination on the metal surface as a probable cause of the inhibition, the idea was to screen Ru-based bimetallic catalysts for their influence on the catalyst activity. First of all, an initial screening of carbon-supported bimetallic phases based on ruthenium with iron, nickel, gallium, indium, tin, bismuth, palladium and platinum, respectively, was carried out (Fig. 3a). The activity and selectivities of the different bimetallic catalysts vary significantly. Overall, all tested catalysts showed a lower performance in the amination of isomannide compared to the benchmark Ru/C catalyst. While for all catalysts at least the monoamines 3 and 4 are formed in significant amounts, the bimetallic cata-

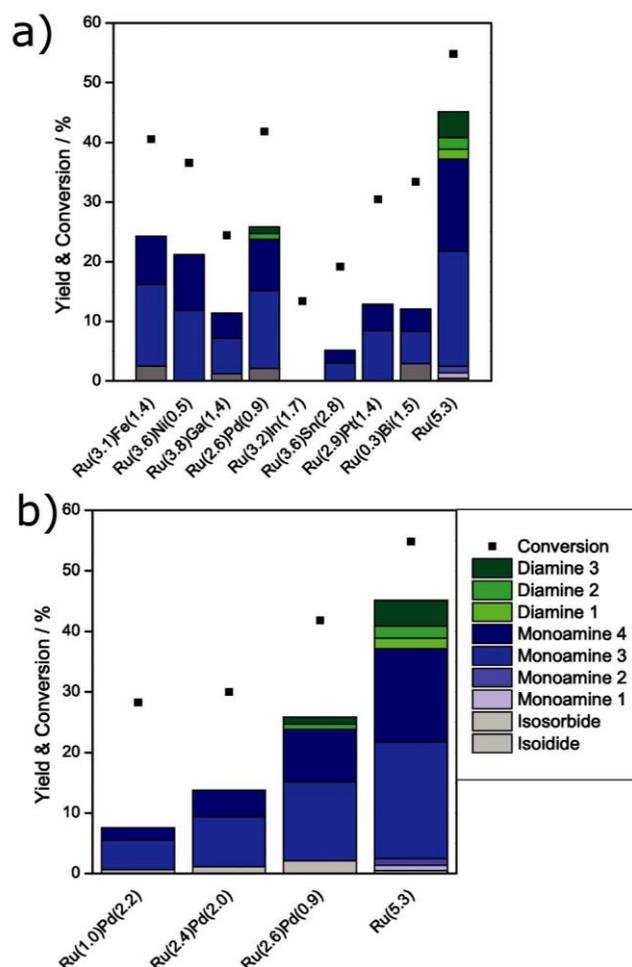


Fig. 3 (a) Screening of different bimetallic ruthenium-based catalysts supported on carbon; (b) results of the amination with bimetallic RuPd/C catalysts with different metal ratios. The values in brackets are the amount of Ru (wt%) on the catalysts as determined by ICP-OES elemental analysis.

lyst with indium apparently inhibits the formation of amines at all. The nickel-, tin- and platinum-based catalysts are more selective towards the amine formation since no isomerization products were detected. This is very important because a more selective conversion albeit the lower activity could be beneficial for further process development.

Compared to the Ru/C benchmark catalyst only the palladium-based bimetallic catalyst yielded diamines at all. Hence, for this bimetallic system a more detailed study was carried out comparing different ratios of ruthenium and palladium supported on the same activated carbon material. A direct dependence of the catalyst activity from the metal ratio was found (Fig. 3b). With decreasing palladium content the conversion and the yield of amines increase. Representatively for the materials prepared by exactly the same procedure the catalyst Ru(2.4)Pd(2.0)/C was investigated by high-angle annular dark field-scanning transmission electron microscopy (HAADF-STEM) coupled with energy-dispersive X-ray spectroscopy (EDX) (Fig. S5 and S6†). Metallic nano-particles with a diameter <7 nm are present with a rather broad particle size distribution. EDX measurement showed the presence of alloyed Ru–Pd particles as well as particles of the individual elemental metals. Apparently, under the applied reaction conditions the available ruthenium surface is crucial for the amination reaction to occur. These first screening experiments for bimetallic Ru-based catalysts and alloy formation showed no beneficial effect in terms of product inhibition and overall catalytic activity. This implies that future process development for the aqueous phase amination of sugar alcohols should focus on supported Ru-catalysts with an optimized dispersion for a maximum accessible Ru metal surface.

Aqueous phase amination of other alcohols

Considering the ability to carry out the amination of hydroxyl groups with ammonia and a solid catalyst in aqueous solutions the transferability of these conditions is of utmost importance regarding the utilization of bio-renewable alcohols. Hence, the amination of various aliphatic primary and secondary as well as mono- and diols was investigated using the commercially available Ru/C benchmark catalyst (Scheme 1). Ethanol was used as an example for a primary alcohol and non-biogenic cyclohexanol as a secondary alcohol. Additionally, various other bi-functional alcohols were selected that can be obtained from bio-renewables, such as propane-1,2-diol, propane-1,3-diol, butane-1,4-diol, butane-2,3-diol, pentane-1,5-diol, and hexane-1,6-diol.⁴⁴ Most of these alcohols are potential diol monomers for polyesters but also as intermediates for diamines to produce, e.g., polyamides. They are partially accessible by fermentation, typically carried out in aqueous solutions, or alternatively by novel chemocatalytic aqueous phase routes.⁴⁵ Hence, an aqueous phase amination process offers a great opportunity for a one-pot transformation of the alcohols to avoid the energy consuming intermediate separation from water.

The screening was carried out using quantitative ¹H NMR spectroscopy (Fig. 4a, S7 and S8†). The mixtures were quanti-

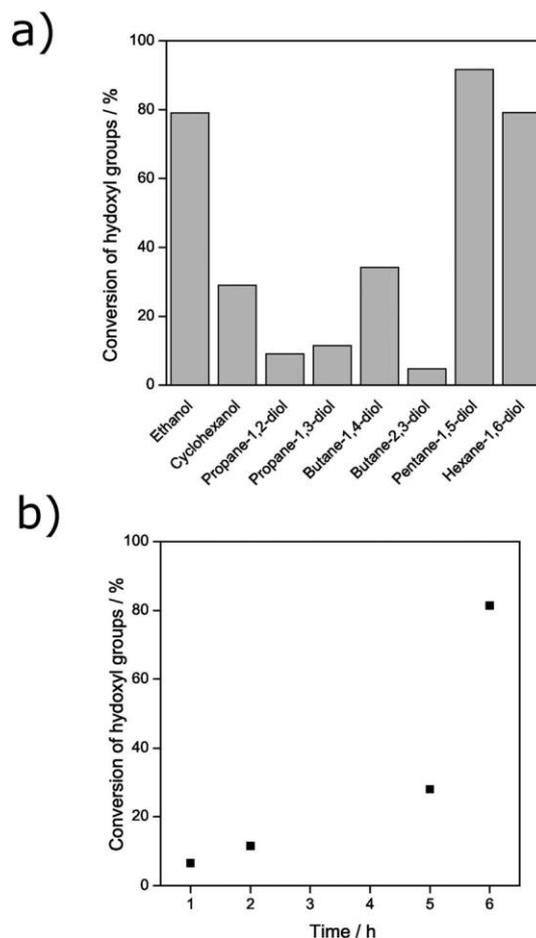


Fig. 4 (a) Conversion of the hydroxyl groups in the aqueous phase of various alcohols (170 °C, 6 h, 500 rpm); (b) time dependence of the conversion of the aqueous phase amination of ethanol.

fied based on the signals of the protons attached to the α -carbon atoms of the hydroxyl and amine groups, respectively. Depending on the substrates a strongly varying catalytic activity was observed with amination yields between 10 and 90%. The amination of ethanol shows one of the highest conversions of up to 80%. Due to overlapping NMR signals the formation of di- and triethylamine as by-products cannot be ruled out although it is feasible since the initially formed primary amine is more reactive than ammonia. This is verified by first insights into the kinetics of the reaction. Therefore, a time resolved study based on batch experiments of varying duration was carried out (Fig. 4b). Based on the quantification method a rather continuous increase in the overall amine yield is observed in the first few hours. After 5–6 h a significant increase is observed. This points towards two different reactions that occur: (I) the initial formation of primary amines, and (II) the subsequent reaction of these amines with alcohols to secondary and tertiary amines. Within the investigated duration of the reaction no equilibrium restrictions seem to limit the reaction. This again implies the different behavior compared to the bifunctional isomannide-based diamine that is

able to strongly bind to the metal surface while mono-functional amines obviously do not show this drawback.

Cyclohexanediol as a model compound for an aliphatic secondary alcohol exhibits under the same reaction conditions a much lower reactivity. A conversion of hydroxyl groups of only 29% is observed while propane-1,2- and -1,3-diol as well as butane-2,3-diol only show conversions below 10%. Especially for the secondary alcohols as substrates the formation of secondary and tertiary amines is less likely due to a higher steric hindrance.

The feasibility of formation of a 6-membered ring explains the high conversion of 90% of pentane-1,5-diol with an intra-molecular ring closure. After a one-fold amination the ring closure occurs during the N-alkylation reaction resulting in the formation of a thermodynamically favored piperidine 6-membered ring with a selectivity of 95%. In this special case the production of piperidine has been mentioned before in the patent literature based on copper and nickel catalysts for reactions in the gas phase.^{46,47} Nevertheless, the option to carry out the reaction in the liquid aqueous phase is still highly advantageous.

The same effect was observed for the amination of hexane-1,6-diol to hexamethylenediamine; a monomer of great industrial importance in the production of Nylon 66. A conversion of hydroxyl groups of up to 79% was observed. As a by-product the 7-membered heterocyclic alkyl amine azepane was found. The production of hexamethylenediamine from hexane-1,6-diol was used in the past by Celanese in an industrial process until 1981.⁴⁸ Also Evonik filed a patent for this direct route based on Cu–Ni–Co catalysts supported on ZrO₂.⁴⁹ However, both processes require a comparatively high hydrogen pressure of up to 300 bar.^{48,49} Hence, based on the option to carry out the amination in the aqueous phase with Ru/C as the solid catalyst high potential for efficient processing conditions is revealed.

Conclusions

In conclusion, we have presented the successful one-pot amination of various biogenic alcohols using Ru/C as a solid catalyst. The influence of the catalyst was investigated in detail based on the amination of the sugar-based diol isomannide. In particular, the feasibility of using other support materials, that are stable under the hydrothermal and basic conditions, was proved. Also, it was shown that the activity and selectivity is significantly influenced by using Ru-based bimetallic catalysts, although elemental Ru/C is the most productive one.

Most importantly, however, the reported catalytic systems allow for the amination of primary and secondary alcohols at temperatures below 200 °C and in aqueous solution. The comparably low temperatures are of great interest for biogenic sugar-based alcohols that often suffer from a limited thermal stability. Being able to conduct the reaction in water as the solvent is essential regarding a holistic process development and considering the fact that many biogenic alcohols can or have to be produced in aqueous solutions. Hence, avoiding

one separation step of the alcohol intermediate from water is essential for the energy efficiency of such a process. Thereby, a new access route towards biogenic amines especially for mono-mers of novel bio-polyamides is exploited.

Is water a suitable solvent for the catalytic amination of alcohols? For this route it can be answered with a “yes”. Although it has to be considered that a suitable purification is required to recycle or to dispose of the water after the process especially regarding residual amines and ammonia. Overall, more detailed research on the influence of the reaction conditions, elucidation of the kinetics and proof of concept for continuous processing are essential for future process development. Also the efficiency and environmental impact of the aqueous phase amination process have to be evaluated to assess and compare its performance regarding the principles of green chemistry and engineering. This issue is addressed in ongoing work especially regarding an overall mass balance, waste amounts and the overall energy requirements that can only be assessed with technical reliable data for the combined reactor and a suitable downstream processing.

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References

- 1 A. B. van Gysel and W. Musin, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2005.
- 2 S. A. Lawrence, *Amines: Synthesis, Properties and Application*, Cambridge University Press, Cambridge, 2004.
- 3 K. S. Hayes, *Appl. Catal., A*, 2001, 221, 187–195.
- 4 K.-i. Shimizu, *Catal. Sci. Technol.*, 2015, 5, 1412–1427.
- 5 M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, 349, 1555–1575.
- 6 C. Gunanathan and D. Milstein, *Angew. Chem., Int. Ed.*, 2008, 47, 8661–8664.
- 7 J. C. Serrano-Ruiz, R. Luque and A. Sepulveda-Escribano, *Chem. Soc. Rev.*, 2011, 40, 5266–5281.
- 8 P. Gallezot, *Chem. Soc. Rev.*, 2012, 41, 1538–1558.
- 9 V. Froidevaux, C. Negrell, S. Caillol, J.-P. Pascault and B. Boutevin, *Chem. Rev.*, 2016, 116, 14181–14224.
- 10 M. Winnacker and B. Rieger, *Macromol. Rapid Commun.*, 2016, 37, 1391–1413.
- 11 I. Delidovich, P. J. C. Hausoul, L. Deng, R. Pfützenreuter, M. Rose and R. Palkovits, *Chem. Rev.*, 2016, 116, 1540–1599.

- 12 M. Pera-Titus and F. Shi, *ChemSusChem*, 2014, 7, 720–722.
- 13 J.-Q. Li and P. G. Andersson, *Chem. Commun.*, 2013, 49, 6131–6133.
- 14 M. Haniti, S. A. Hamid, C. L. Allen, G. W. Lamb, A. C. Maxwell, H. C. Maytum, A. J. A. Watson and J. M. J. Williams, *J. Am. Chem. Soc.*, 2009, 131, 1766–1774.
- 15 S. Bähn, S. Imm, L. Neubert, M. Zhang, H. Neumann and M. Beller, *ChemCatChem*, 2011, 3, 1853–1864.
- 16 A. M. Rasero-Almansa, A. Corma, M. Iglesias and F. Sánchez, *ChemCatChem*, 2014, 6, 1794–1800.
- 17 A. Peeters, L. Claes, I. Geukens, I. Stassen and D. De Vos, *Appl. Catal., A*, 2014, 469, 191–197.
- 18 S. P. Shan, T. T. Dang, A. M. Seayad and B. Ramalingam, *ChemCatChem*, 2014, 6, 808–814.
- 19 A. Mehta, A. Thaker, V. Londhe and S. R. Nandan, *Appl. Catal., A*, 2014, 478, 241–251.
- 20 D. Pingen, C. Müller and D. Vogt, *Angew. Chem., Int. Ed.*, 2010, 49, 8130–8133.
- 21 D. Pingen, O. Diebolt and D. Vogt, *ChemCatChem*, 2013, 5, 2905–2912.
- 22 S. Imm, S. Bähn, M. Zhang, L. Neubert, H. Neumann, F. Klasovsky, J. Pfeffer, T. Haas and M. Beller, *Angew. Chem., Int. Ed.*, 2011, 50, 7599–7603.
- 23 M. H. S. A. Hamid, P. A. Slatford and J. M. J. Williams, *Adv. Synth. Catal.*, 2007, 349, 1555–1575.
- 24 D. Pingen, M. Lutz and D. Vogt, *Organometallics*, 2014, 33, 1623–1629.
- 25 X. Ye, P. N. Plessow, M. K. Brinks, M. Schelwies, T. Schaub, F. Rominger, R. Paciello, M. Limbach and P. Hofmann, *J. Am. Chem. Soc.*, 2014, 136, 5923–5929.
- 26 K.-i. Shimizu, K. Kon, W. Onodera, H. Yamazaki and J. N. Kondo, *ACS Catal.*, 2013, 3, 112–117.
- 27 K.-i. Shimizu, N. Imaiida, K. Kon, S. M. A. H. Siddiki and A. Satsuma, *ACS Catal.*, 2013, 3, 998–1005.
- 28 K.-i. Shimizu, S. Kanno, K. Kon, S. M. A. Hakim Siddiki, H. Tanaka and Y. Sakata, *Catal. Today*, 2014, 232, 134–138.
- 29 X. Cui, X. Dai, Y. Deng and F. Shi, *Chem. – Eur. J.*, 2013, 19, 3665–3675.
- 30 T. Takanashi, Y. Nakagawa and K. Tomishige, *Chem. Lett.*, 2014, 43, 822–824.
- 31 R. Pfützenreuter and M. Rose, *ChemCatChem*, 2016, 8, 251–255.
- 32 M. Rose and R. Palkovits, *ChemSusChem*, 2012, 5, 167–176.
- 33 M. Tatarkhanov, E. Fomin, M. Salmeron, K. Andersson, H. Ogasawara, L. G. M. Pettersson, A. Nilsson and J. I. Cerdá, *J. Chem. Phys.*, 2008, 129, 154109.
- 34 J. Tan, J. Cui, T. Deng, X. Cui, G. Ding, Y. Zhu and Y. Li, *ChemCatChem*, 2015, 7, 508–512.
- 35 A. Michaelides, A. Alavi and D. A. King, *J. Am. Chem. Soc.*, 2003, 125, 2746–2755.
- 36 S. Maier, I. Stass, J. I. Cerdá and M. Salmeron, *Phys. Rev. Lett.*, 2014, 112, 126101.
- 37 P. J. Feibelman, *Science*, 2002, 295, 99–102.
- 38 D. N. Denzler, S. Wagner, M. Wolf and G. Ertl, *Surf. Sci.*, 2003, 532–535, 113–119.
- 39 C. Michel and P. Gallezot, *ACS Catal.*, 2015, 5, 4130–4132.
- 40 S. Wuyts, D. E. De Vos, F. Verpoort, D. Depla, R. De Gryse and P. A. Jacobs, *J. Catal.*, 2003, 219, 417–424.
- 41 J. Le Nôtre, J. van Haveren and D. S. van Es, *ChemSusChem*, 2013, 6, 693–700.
- 42 W. Henry, *Philos. Trans. R. Soc. London*, 1803, 93, 29–274.
- 43 L. Wang and F.-S. Xiao, *ChemCatChem*, 2014, 6, 3048–3052.
- 44 M. Pera-Titus and F. Shi, *ChemSusChem*, 2014, 7, 720–722.
- 45 K. Wagemann, *ChemBioEng Rev.*, 2015, 2, 315–334.
- 46 F. Haese, A. Böttcher, B. Stein, W. Reif, J.-P. Melder, K.-H. Ross, H. Rütter, S. Liang and S. Rittinger, *WO 2005110969A1*, 2005.
- 47 K. V. Raghavan, S. J. Kulkarni, R. R. Vippagunta and S. Nagabandi, *WO 02079160A1*, 2002.
- 48 K. Weissermel and H.-J. Arpe, in *Industrial Organic Chemistry*, Wiley-VCH Verlag GmbH, 2008, pp. 15–57, DOI: 10.1002/9783527619191.ch2.
- 49 F.-E. Baumann, A. Martin, M. Ullrich, M. Roos, P. Hannen, F.-M. Petrat, H. Häger, A. Köckritz, G. Walther and J. Deutsch, *EP 2484659B1*, 2014.