Pd-catalyzed decarboxylation of glutamic acid and pyroglutamic acid to bio-based 2-pyrrolidone

Pd-catalyzed Decarboxylation of Glutamic Acid and Pyroglutamic Acid to Bio-based 2-Pyrrolidone

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In order to recycle nitrogen from nitrogen-rich waste streams, particularly protein waste, we studied the decarboxylation of pyroglutamic acid and glutamic acid in a one-pot reaction to bio-based 2-pyrrolidone. After screening of a wide range of supported Pd and Pt catalysts, 5 wt% Pd/Al_2O_3 displayed the highest yield (70%) and selectivity (81%) for the decarboxylation of pyroglutamic acid in water at 250°C and under inert atmosphere. Side products originate from consecutive reactions of 2-pyrrolidone; different reaction pathways are proposed to explain the presence of degradation products like propionic acid, γ-hydroxybutyric acid, γ-butyrolactone and methylamine. An extensive study of the reaction parameters was performed to check their influence on selectivity and conversion. This heterogeneous catalytic system was successfully extended to the conversion of glutamic acid.

Introduction

Nitrogen is a biologically essential element for the synthesis of nucleotide and amino acid building blocks in living organisms, as well as an essential constituent of many commodity chemicals (solvents, bases, polymers etc.). Currently, the Haber-Bosch process is the main entry of nitrogen into biobased and fossil-derived molecules: ammonia is a major resource for plant fertilizer formulation and nitrogen-containing organic chemicals production.[1] The increasing demand to sparingly use energy and resources is forcing the exploitation of alternative and sustainable sources of energy, fuels and chemicals.[2] Biomass constituents containing C, H and O in waste streams, particularly carbohydrates and lipids, have been extensively studied as a potential renewable resource for chemicals production.[3-5] Meanwhile, the nitrogen-containing protein fraction has received only little attention so far. Nevertheless, exemplary biomass streams, like dried distiller grains with solubles (DDGS) from wheat or maize,[7,8] sugarbeet and sugarcane vinasse, poultry feather meal[9] or press cakes from castor oil production[10] contain up to 20-40 wt% of proteins;[11] the amino acid constituents can be chemically modified into amines, amides, nitriles etc.[12] Until now, protein waste is mainly processed into animal feed. However, the Ncycle is rather inefficient because a large fraction of the nonessential nitrogen is excreted by animals and lost to the soil with additional production of the greenhouse gas N_2O.

Therefore, recycling of nitrogen from protein residuals to chemicals could result in a more efficient closure of the Ncycle, and in a strong decrease in energy and environmental impact.[1]

Glutamic acid is the most abundant amino acid constituent in plant biomass.[11] It is therefore highly attractive for producing industrially relevant bio-based chemicals, for instance 3-cyanopropionate[13], which is an intermediate to acrylonitrile[14] and succinonitrile[15] by chemocatalysis, or γ-aminobutyric acid via enzymatic decarboxylation.[16] The latter can be converted further to pyrrolidones.[17] In addition, from pyroglutamic acid, which is the cyclic condensation product, one can obtain pyroglutaminol and prolinol by Ru-catalyzed

hydrogenation,[18] and succinimide by oxidative decarboxylation on Ag catalysts.[19] The latter reaction, however, uses potassium persulfate as oxidant, producing a large amount of salt waste.

This inspired us to develop a chemocatalytic system for the decarboxylation of pyroglutamic acid to 2-pyrrolidone, a valuable industrial solvent and a precursor for *N*vinylpyrrolidone [17] and new non-reprotoxic *N*-alkyl pyrrolidones.[20] Pyroglutamic acid is formed very fast at elevated temperatures (> 120°C),[21] and might be present in biomass streams after high-temperature processing. Direct decarboxylation of pyroglutamic acid to 2-pyrrolidone using metal catalysts, in a reaction similar to the known fatty acid decarboxylation to paraffinic hydrocarbons,[22-26] can offer a great bio-based alternative to the current petrochemical pathway to pyrrolidones. A reported bio-based method for the production of pyrrolidones from glutamic acid involves a twostep process: an enzymatic decarboxylation to γ-aminobutyric acid followed by cyclization at elevated temperatures.[17] However, high enzyme activity requires a rather strict pH control and sufficient supply of an expensive pyridoxal phosphate co-factor.

This paper discloses a chemocatalytic route to decarboxylate pyroglutamic acid or glutamic acid in a one-pot reaction to bio-based 2-pyrrolidone with supported Pd catalysts in water, at 250°C and under inert atmosphere. Both the solvent and the substrate are radically different from those of the known fatty acid decarboxylation, which made us decide to screen a much wider range of supports and metals than the most performant reported catalysts. In addition, both pH and temperature will be varied to check their influence on selectivity and conversion.

Experimental

Support synthesis

Besides carbon, various oxide powders were used as supporting materials. High surface area (HSA) spinel-type materials, HSA$MgAl_2O_4$, HSA-$BaAl_2O_4$ and HSA-$CaAl_2O_4$, were synthesized according to literature procedures.[27,28] An aqueous solution of respectively $Mg(NO_3)_2.6H_2O$, $Ba(NO_3)_2$ or $Ca(NO_3)_2.4H_2O$ together with $Al(NO_3)_3.9H_2O$ (M^{2+}/Al^{3+} = 0.5) was mixed with poly(vinyl alcohol), with a molar ratio of metal ions to alcohol groups of 1. The mixture was stirred at 50°C till complete dissolution. The pH was adjusted to 10 with ammonia (25 wt% in water). Next, the suspension was stirred for 3 h and aged overnight. The precipitate was washed thoroughly with water and lyophilized afterwards, leading to a fine powder. Finally, the spinels were obtained after calcination at 800°C (8 h, 3°C/min).

Catalyst synthesis

The metal loading of both commercial and self-prepared catalysts was 5 wt%. Pd-based catalysts were synthesized by impregnating the supports with an aqueous solution of $PdCl_2$ and a minimal amount of HCl to ensure precursor dissolution. Impregnated supports were dried overnight at 60°C. Finally, the catalysts were calcined at 400°C (30 min, 2°C/min, 100 ml/min O_2) and reduced at 300°C (1 h, 2°C/min, 100 ml/min H_2) in a quartz U-tube. Pd/Al_2O_3 was also prepared by incipient wetness impregnation with a $Pd(NH_3)_4Cl_2.H_2O$ precursor to verify the effect of the Pd precursor, but similar results were obtained as with $PdCl_2$. Pt/Al_2O_3 was produced by incipient wetness impregnation with a $Pt(NH_3)_4Cl_2.H_2O$ precursor and dried overnight at 60°C.

Next, the material was calcined at 400°C (1 h, 2°C/min, 100 ml/min O_2) and reduced at 400°C (1 h, 2°C/min, 100 ml/min H_2) in a quartz U-tube.

Catalyst characterization

Powder X-ray diffraction (XRD) measurements were collected on a STOE STADI P diffractometer equipped with an image plate detector using CuK α radiation and Debye-Scherrer geometry. Nitrogen physisorption measurements were performed by using a Micromeritics 3Flex surface analyzer at 77 K. Before the measurement, the 100 mg samples were outgassed at 423 K for 6 h under vacuum. High angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed for Pd loaded Al_2O_3, SiO_2, ZrO_2 and $MgAl_2O_4$ using a FEI Tecnai operated at 200kV. In case of the sample where Pd is deposited on ZrO_2, the contrast in the HAADF-STEM images was too small and energy dispersive X-ray (EDX) spectroscopy was applied. To determine acidic and basic properties of the different catalysts, 50 mg of the different catalysts were suspended in 3 ml H_2O, stirred for 6 h after which the pH was measured. Characterization data are available in the Supporting Information.

Reaction

All reactions were performed in a 50 ml high-pressure Parr batch reactor (Series 5500; Type SS-316; Model 4848 temperature controller). In a typical reaction, the reactor was charged with the substrate (4 mmol), water (20 ml) and the noble metal catalyst (metal/substrate = 4 mol%). The reactor was sealed, purged 6 times with N2 while stirring and finally pressurized with 6 bar N2 at room temperature. Next, the reactor was heated to 250°C (except for the temperature variation experiments). During the heating step (20 min), the pressure increased to 40 bar at 250°C. After 6 h, heating was stopped and the reactor was allowed to cool down. The solid catalyst was removed by centrifugation and the reaction mixture was analyzed by NMR and HPLC. For time-controlled experiments, the catalyst loading was reduced (metal/substrate = 2 mol%) to verify initial reaction products in more detail; time recording started when 250°C was reached and the reaction was terminated by fast cooling with water and ice. To study the effect of the pH on the conversion of pyroglutamic acid and glutamic acid, a Teflon liner was loaded with the pyroglutamic acid or glutamic acid solution (0.2 M in water (15 ml)), adjusted to a certain pH with H_3PO_4 or NaOH, and the solid noble metal catalyst (metal/substrate = 4 mol%). The Teflon liner was inserted into the reactor and the standard reaction procedure was applied.

Product analysis and identification

Reaction mixtures were analyzed by ^{1}H-NMR spectroscopy to quantify the product yields as well as by HPLC for conversion determination. In order to determine product yields with ^{1}HNMR, DMSO (δ = 2.7 ppm, s, 6H) was added as an external standard to the reaction mixture. The NMR samples were prepared by diluting 300 µl of the reaction mixture containing external standard with 300 µl of D_2O. ^{1}H-NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer equipped with a BBI 5 mm probe. The broad water signal in the ^{1}H-NMR spectra was suppressed by applying an adapted pulse program: p1 8 µs; pl1 -1 db; pl9 50 db; o1P on the resonance signal of water, determined from the previous 1H-NMR measurement: ds 2; ns 32; d1 5 s; aq 2.55 s; sw 16. The conversion of pyroglutamic acid was determined by HPLC, because quantification by ^{1}H-NMR was

inaccurate as a result of deuterium exchange with the acidic proton on the ⟨-carbon and, hence, a decreased NMR signal at δ = 4.1-4.2 ppm (t, J = 8 Hz, ^{1}H).[21] The conversion of pyroglutamic acid was directly calculated from HPLC output data recorded on an Agilent SL 1200 binary system equipped with a ZORBAX ECLIPSE Plus C18 column (4.6 x 250 mm, 5 μm particles) and a UV detector (212 nm). The mobile phase was a combination of H_2O/acetic acid (1 v%) and acetonitrile with a gradient elution profile. Product identification was also performed with gas chromatography coupled to a mass spectrometer (GC-MS), using an Agilent 6890 GC, provided with a HP-5ms column and coupled to a 5973 MSD mass spectrometer, and additionally by 2D ^{1}H-^{13}C-NMR and ^{15}N-NMR spectroscopy, respectively on a Bruker Avance 400 MHz spectrometer equipped with a BBI 5 mm probe and a Bruker Avance 2 plus 600 MHz spectrometer equipped with a BBO 5 mm probe. The composition of the gas phase after reaction (with Pd/ZrO_2) was analyzed by GC, using an Interscience TraceGC equipped with a Hayesep Q and a Molsieve 5A column connected to a thermal conductivity detector (TCD) and a Rtx-1 column connected to a flame ionization detector (FID). Thermodynamic calculations of side reactions were performed with Aspen Plus® software; a detailed description is given in the Supporting Information.

Results and discussion

Initial experiments with Pd/C and Pd/Al_2O_3

In the context of biomass deoxygenation for the production of biodiesel, direct decarboxylation with metallic heterogeneous catalysts has already been investigated for the conversion of fatty acids to hydrocarbons under inert atmosphere, or in the presence of a minor H2 pressure.[24,26] With stearic acid as a model reactant, Snåre *et al.* have tested the decarboxylation activity of Ni, $NiMoO_x$, Ru, Pd, Pt, Ir, Os and Rh supported on silica, alumina, active carbon and several alloys. Pd and Pt supported on carbon were identified as the most promising catalysts for this reaction at 300°C.[25] The direct decarboxylation of fatty acids is mostly performed in highboiling organic media, like *n*-dodecane; reports on this reaction in aqueous media are scarce. However, according to the principles of green chemistry,[29] water is highly preferable for the decarboxylation of (pyro)glutamic acid, which additionally will often be available as aqueous solutions. Until now, hydrothermal decarboxylation of fatty acids has been reported under near- or supercritical water conditions.30 Pt/C and Pd/C are able to catalyze this reaction at temperatures > 330°C.[22,23] However, these conditions will probably be too severe to preserve other functionalities in amino acids. In addition, arylcarboxylic acids[31] and very recently also itaconic acid[32] have been successfully decarboxylated in water with Pd- and Pt-based catalysts at 250°C and 40-50 bar of N_2 and steam. As carbon supported Pd and Pt were demonstrated to be the best catalysts for decarboxylations in organic solvents[25] as well as in water,[22,23,32] we decided in an initial experiment to expose pyroglutamic acid to a Pd/C catalyst in water at 250°C under 40 bar of N_2. After 6 h, quantitative analysis showed that 2- pyrrolidone was formed with a yield of 56% at a pyroglutamic acid conversion of 83%. Ford *et al.* showed that, compared to Pd/C, Pd/Al_2O_3 has an even higher initial decarboxylation activity for the fatty acids; however, the catalyst deactivated rapidly in organic solvents.[33] Therefore, pyroglutamic acid was also exposed to a Pd/Al_2O_3 catalyst under identical conditions as for the Pd/C catalyst. This yielded already 70% of 2- pyrrolidone at a pyroglutamic acid conversion of 85%, which confirmed the excellent decarboxylation activity.

Next, cyclopentanecarboxylic acid was reacted under the same conditions as pyroglutamic acid with the Pd/Al_2O_3 catalyst. However, only 8% of cyclopentanecarboxylic acid was converted to cyclopentane. This suggests that the amide group in pyroglutamic acid, which is electron-withdrawing relative to the carboxylic acid, might be required for a high decarboxylation rate. The amide group might also enhance the adsorption of pyroglutamic acid on the catalytic sites compared to cyclopentanecarboxylic acid and consequently induce a higher decarboxylation rate.

Side product formation

In the decarboxylation of pyroglutamic acid on Pd/C or Pd/Al_2O_3, besides 2-pyrrolidone, several side products were identified by GC-MS and ^{1}H-NMR (Supporting Information): propionic acid (PA), γ-hydroxybutyric acid (GHB), γ- butyrolactone (GBL) and pyrrolidine, with yields of 12%, 4%, 2% and < 1% respectively. In addition, 2D coupled ^{1}H-^{13}CNMR and ^{15}N-NMR measurements confirmed the formation of another side product, of which the spectroscopic signatures agree with those of methylamine. The 2D coupled ^{1}H-^{13}C-NMR measurements showed a coupled signal between a ^{13}C atom at δ = 33 ppm and a ^{1}H atom at δ = 2.4 ppm. The ^{15}N-NMR measurements on the product mixture showed besides the expected signal at δ = -258 ppm, which can be attributed to the lactam, another clear signal at δ = -361 ppm, which is consistent with the formation of an alkylamine like methylamine.[34] In principle, one could also expect the further decarboxylation of propionic acid to ethane, although decarboxylation of free carboxylic acids, like fatty acids, would require temperatures above 250°C. To check whether or not ethane is formed, propionic acid was treated under identical reaction conditions. Only low conversion of propionic acid (< 2%) was observed. After gas-phase analysis of the reaction with pyroglutamic acid, only traces of ethane were found. Therefore, the formation of ethane as a consequence of propionic acid decarboxylation can be neglected. To clarify whether propionic acid is produced from either pyroglutamic acid or from 2-pyrrolidone, the yields of both propionic acid and 2-pyrrolidone were measured as a function of time (Figure 1). Immediately after heating the reactor up to 250°C, small amounts of propionic acid were detected, next to 2-pyrrolidone, suggesting that propionic acid is at least partially formed directly from pyroglutamic acid. However, after 2 h one observes a decrease of the 2-pyrrolidone selectivity and an increase of the propionic acid selectivity, which indicates that propionic acid is also formed in a consecutive reaction from 2-pyrrolidone. After the first 2 h, the rate of pyroglutamic acid conversion started to slow down and the formation of propionic acid was significant. Minor amounts of GHB, GBL and pyrrolidine were only observed upon prolonged heating, indicating that they are produced by consecutive reactions as well. To confirm the origin of these side products, 2-pyrrolidone was subjected to identical reaction conditions as pyroglutamic acid. Propionic acid, methylamine, GHB, GBL and pyrrolidine but also butyric acid were observed in the reaction of 2-pyrrolidone, confirming that most side products originate from 2-pyrrolidone rather than directly from pyroglutamic acid. Remarkably, in the decarboxylation of pyroglutamic acid, the selectivity for 2-pyrrolidone increased at short reaction times, reaching a maximum after 1-2 h. This might be explained by the pH change during the early stage of the reaction: the pH increased from 1.8 in the initial pyroglutamic acid solution, to 5 at 85% conversion, because basic amine by-products are formed.

It is important to note that noble metals (Pt, Ru, Rh, Pd etc.) are able to catalyze aqueous reforming in the same temperature range as decarboxylation (200°C-250°C). During aqueous reforming, oxygenated molecules, in particular alcohols and aldehydes,[35,36] are reformed to lower hydrocarbons, CO and H_2 in a complex network of dehydration, dehydrogenation, hydrogenation, C-C cleavage and C-O cleavage reactions.[37] Bearing this in mind, a reaction scheme explaining the byproduct formation can be proposed (Scheme 1). First, the lactam product is hydrolyzed to a γ-amino acid; this step is catalyzed by a Lewis acid or by a base. The resulting amine group is easily dehydrogenated to an imine under inert atmosphere over the Pd catalyst. Due to the excess of water and the acidic conditions, this imine is readily hydrolyzed to form an aldehyde and ammonia. This aldehyde is probably rather present as a reactive intermediate, activated at the catalyst surface by the formation of a Pd-C or Pd-O bond.[37] The presence of such an intermediate provides access to two of the observed side products: on the one hand it could react to propionic acid and CO by decarbonylation (C-C cleavage). On the other hand it could be hydrogenated to the corresponding alcohol, GHB. Subsequently, GHB can undergo cyclization to form GBL and H_2O, as expected at this high temperature;[17] or the alcohol group can be hydrogenolyzed in the presence of H_2 to form butyric acid. Many of these side products could further degrade to lower, volatile hydrocarbons, CO and H_2. This would explain the increasing mass imbalance and thus a stronger decrease in the selectivity of 2-pyrrolidone in time. After 2 h, only 7 mol% of the converted pyroglutamic acid could not be accounted for, at a conversion of 60%; this increased to 18 mol% after 8 h, at a conversion of 93%.

Furthermore, aqueous reforming reactions at these temperatures and with these catalysts are often accompanied by the water-gas shift (WGS) reaction.[37,38] In this way CO, from the aqueous reforming reaction, can react with water on the metal catalysts to generate H_2 and CO_2:

$$CO + H_2O \leftrightharpoons CO_2 + H_2 \quad (1)$$

The production of H_2 in the water-gas shift reaction and aqueous reforming can thus contribute to the formation of butyric acid and can also explain the reduction of 2-pyrrolidone to pyrrolidine (Scheme 1). This was confirmed by adding 20 v% of H_2 to the reaction atmosphere at room temperature, which yielded 9% of pyrrolidine after 6 h, compared to < 1% in the absence of H_2. By gas-phase analysis, besides CO_2, a significant amount of H_2 was detected. The quantity of CO was below the detection limit of the detector, due to the position of the water-gas shift equilibrium (1) towards CO_2 and H_2.

Combining the previous reactions, viz. the degradation of 2- pyrrolidone to propionic acid together with the water-gas shift reaction, one could obtain:

$$\text{Pyrrolidone} + 3H_2O \rightarrow NH_3 + PA + CO_2 + 2H_2 \quad (2)$$

However, next to the water-gas shift reaction, part of the CO could also be hydrogenated to formaldehyde,[39] which can react with NH_3 and H_2 to methylamine. The degradation of 2-pyrrolidone to propionic acid could then be rewritten as:

$$\text{Pyrrolidone} + H_2O \rightarrow PA + H_2C = NH \quad (3)$$

with H_2C=NH as the imine derived from formaldehyde. Combining twice reaction (3) and once reaction (2), thereby including imine hydrogenation, provides the following overall reaction:

$$3\ \text{Pyrrolidone} + 5H_2O \rightarrow 3\ PA + NH_3 + CO_2 + 2CH_3NH_2 \quad (4)$$

While equation (4) does not intend to be representative of the precise stoichiometry of the overall process, it nevertheless clearly shows that the degradation of 2-pyrrolidone under inert atmosphere, with formation of propionic acid, can be accompanied by hydrogen formation, which is needed to explain the formation of a reduced compound like methylamine. In order to substantiate the feasibility of reactions (2) and (4), thermodynamic calculations were performed (Supporting Information). According to these calculations, both for reactions (2) and (4), the thermodynamic equilibrium is strongly in favor of the products. Furthermore, δ-valerolactam (C_5) and ε-caprolactam (C_6) were subjected to the same conditions as 2-pyrrolidone (Table 1).

In both reactions the corresponding C_{n-1} acid was the main product. Moreover, the yield of the corresponding C_{n-1} acid increases with the ring size of the lactam.

Catalyst screening

As mentioned before, carbon has often been found to be the best support for the decarboxylation of fatty acids, due to its hydrophobic character, high surface area and thus suitable adsorptive properties.[33] However, when the reaction is performed with smaller and more polar reactants, like pyroglutamic acid, and water is selected as solvent, the optimal support choice could be quite different. Furthermore, supports like Al_2O_3 have a considerably higher isoelectric point than carbon, enabling a Coulombic attraction between the carboxylate group and the Al_2O_3 support in the relevant pH range (1.8-5), which would increase the coverage of the surface with the reactant. A strong improvement was already observed in the initial experiments using Pd/Al_2O_3. Therefore, also other Pd-based catalysts were screened to verify the influence of the support on the activity and the selectivity in the aqueous decarboxylation of pyroglutamic acid. Neutral or even basic supports like $BaSO_4$ and high surface area spinels of $MgAl_2O_4$, $BaAl_2O_4$ and $CaAl_2O_4$, as well as acidic ZrO_2 and SiO_2 supports were tested (Table 2). pH measurements of suspensions of the Pd loaded supports in water demonstrated that the catalysts can influence the acidity or basicity of the system (Supporting Information). Pd/ZrO_2 (yielding a pH of 3.7) and Pd/$MgAl_2O_4$ (pH 8.9) turned out to be the most acidic and basic catalysts respectively. While Pd/$BaAl_2O_4$, Pd/$CaAl_2O_4$ and Pd/$BaSO_4$ are rather neutral or slightly basic materials, Pd/Al_2O_3, Pd/C and Pd/SiO_2 show more acidic properties.

Blank reactions without catalyst, or using metal-free carbon or Al_2O_3 gave almost no conversion; only Al_2O_3 yielded 2-pyrrolidone (3%), indicating that the alumina support is very slightly active. On all metal-loaded catalysts, however, conversions > 60% were reached within 6 h. The three main reaction products were 2-pyrrolidone, propionic acid and methylamine, with only very small amounts of GBL, GHB, pyrrolidine and sometimes butyric acid. Yields and selectivities for 2-pyrrolidone vary significantly among the different catalysts (Table 2). For example, Pd/$MgAl_2O_4$ showed full conversion (> 99%), but the consecutive reaction to

propionic acid was also prominent: the yields of 2-pyrrolidone and propionic acid were 54% and 36%, respectively. Similar effects were observed for Pd/ZrO_2 catalysts, with a 2-pyrrolidone and a propionic acid yield of 57% and 20%, respectively. This could be attributed to the acid-base properties of both catalysts: side product formation is initiated by hydrolysis of the lactam to γ - aminobutyric acid, which is most likely catalyzed by Lewis acid sites or by base (Scheme 1). Furthermore, catalysts with a comparable effect on the pH, e.g. Pd/SiO_2, Pd/Al_2O_3, $Pd/BaSO_4$, $Pd/BaAl_2O_4$ and $Pd/CaAl_2O_4$ show a similar selectivity for 2-pyrrolidone and propionic acid as well. The highest selectivity to 2-pyrrolidone was obtained with the Al_2O_3- and SiO_2-supported catalysts. Decarboxylation with Pd/Al_2O_3 yielded 70% 2-pyrrolidone and only 9% propionic acid; for Pd/SiO_2 the yield was somewhat lower at 48%, but with only 5% of propionic acid, whereby the selectivity to 2-pyrrolidone remained high. Next to the assessment of the acidbase properties of the catalysts, HAADF-STEM imaging was performed in combination with EDX on the Pd/Al_2O_3, Pd/SiO_2, Pd/ZrO_2 and $Pd/MgAl_2O_4$ catalysts (Figure 2), in order to verify how the Pd particle size might influence reaction selectivity and conversion.

The average particle diameter of the Pd clusters on Pd/SiO_2 (8.8 nm) was clearly larger than for Pd/Al_2O_3 (3.7 nm), Pd/ZrO_2 (5.6 nm) and $Pd/MgAl_2O_4$ (6.6 nm); these numbers correspond to rather broad particle size distributions (Supporting Information). This could explain the significantly lower conversion using Pd/SiO_2 in comparison with other supported catalysts. Le Nôtre *et al.* reported high selectivity in the aqueous decarboxylation of itaconic acid to methacrylic acid using a 5 wt% Pt/Al_2O_3 catalyst.[32] Therefore, Pt-based catalysts were evaluated in the decarboxylation of pyroglutamic acid as well (Table 2). Although Pt/Al_2O_3 and Pt/C were highly active, they catalyzed the consecutive reactions to propionic acid and butyric acid to a much larger extent than Pd. Pt-based catalysts are significantly more active for the aqueous-phase reforming reactions.[37-38] This also explains the more pronounced mass imbalance compared to Pd-based catalysts: 9 mol% (Pd/C) vs. 24 mol% (Pt/C), and 6 mol% (Pd/Al_2O_3) vs. 16 mol% (Pt/Al_2O_3). The generation of more CO_2 and H_2 is also evidenced by a stronger pressure increase during the reaction. Consequently, the selectivity to 2-pyrrolidone decreased to 37% and 56% for Pt/C and Pt/Al_2O_3, respectively. Because the highest yield and selectivity were obtained with Pd/Al_2O_3, this catalyst was used in further experiments. In a recycling experiment, the selectivity to 2-pyrrolidone was still 79% and the conversion decreased slightly to 76%. This small loss of activity could probably be attributed to sintering of the small palladium particles at this high temperature.

Effects of temperature and pH; glutamic acid conversion

Low conversions (< 10%) were observed when the reaction was performed below 200°C (Figure 3). Above 225°C significantly higher conversions were measured and the highest yield of 2-pyrrolidone (70%) was obtained at 250°C. The highest selectivity to 2-pyrrolidone (90%) was reached at 225°C, but it dropped significantly to 57% at 275°C. This can be explained by an enhanced aqueous reforming of 2-pyrrolidone and other products (in combination with the water-gas shift reaction) to volatile hydrocarbons, CO, CO_2 and H_2; at 275°C, the amount of non-identified products was 22% based on the initial molar input of pyroglutamic acid.

An attempt was made to use glutamic acid, instead of pyroglutamic acid, as the direct precursor to 2-pyrrolidone. A one-pot process is proposed: in a first non-catalytic step, glutamic acid is converted to

pyroglutamic acid; the pyroglutamic acid intermediate can then be decarboxylated in the presence of the Pd-based catalyst. Under standard reaction conditions, the conversion of glutamic acid was nearly complete after 6 h, whereas the conversion of pyroglutamic acid was only 85% under identical conditions. Moreover, the selectivity to 2-pyrrolidone decreased to 63% compared to 81% when starting from pyroglutamic acid (Figure 4).

These differences in conversion and selectivity are probably the result of a difference in pH of the reaction solution upon pyroglutamic acid formation. In fact, the pH of an aqueous pyroglutamic acid solution is around 1.8, whereas a slightly less acidic pH is obtained at room temperature when pyroglutamic acid is first formed from glutamic acid. These observations suggest an optimal starting pH for achieving the highest yield of 2-pyrrolidone. Therefore the pH in the decarboxylation of pyroglutamic acid was varied by the addition of H_3PO_4 or NaOH; however, any addition of acid or base led to poorer results (Figure 5). Adding NaOH strongly reduced conversion and selectivity to 2-pyrrolidone. In contrast, the formation of both 2-pyrrolidone and propionic acid was suppressed in acidified conditions. The consecutive reaction to propionic acid is more pronounced when the initial pH is above 4 (pH 8.2 after reaction); hydrolysis of the lactam can be enhanced in more basic conditions, initiating the different side reactions. While the addition of acid or base has only adverse effects in the case of pyroglutamic acid, H_3PO_4 increased the yield and selectivity to 2-pyrrolidone when starting from glutamic acid (Figure 6). The degradation to propionic acid was strongly suppressed in acidic conditions.

The optimum for the H_3PO_4 concentration was between 0.075 M and 0.1 M, where almost the same yield and selectivity for 2-pyrrolidone, 72% and 78% respectively, were obtained as when starting from pyroglutamic acid. It is interesting to compare this effect of acidification with the data on pyroglutamic acid conversion of Figure 5. As explained before, when pyroglutamic acid originates from glutamic acid in water, the pH is slightly higher than that of a solution of genuine pyroglutamic acid; by adding H_3PO_4 to glutamic acid, the pH is adjusted to the optimal conditions for decarboxylation of the pyroglutamic acid intermediate, as shown in Figure 5.

Conclusion

The aqueous decarboxylation of pyroglutamic acid and glutamic acid to bio-based 2-pyrrolidone was successfully performed using Pd-based catalysts. Besides the conventional Pd/C, a broad series of supported Pd catalysts was screened for the decarboxylation of pyroglutamic acid. For almost all catalysts high conversions (> 80%) were obtained. Reactions with Pd/Al_2O_3 and Pd/SiO_2 resulted in the highest selectivity (81%) after 6 h at 250°C. With a yield of 70%, Pd/Al_2O_3 is the most performant material for the production of 2-pyrrolidone from pyroglutamic acid. Optimization of the reaction parameters, like temperature and pH, for pyroglutamic acid resulted in a selectivity to 2-pyrrolidone of 90% at 225°C without any pH adjustment, however at moderate conversion. Besides pyroglutamic acid, glutamic acid was successfully converted to 2-pyrrolidone in a one-pot reaction. The addition of 0.1 M H_3PO_4 yielded 72% of 2-pyrrolidone at 250°C after 6 h, with 78% selectivity. The desired bio-based lactam can thus be obtained from either pyroglutamic acid or glutamic acid. This is a

valuable result as glutamic acid is massively available in biomass waste streams[11] or by fermentative production.[40]

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Notes and references

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Electronic Supplementary Information (ESI) available: Catalyst characterization and NMR-data. See DOI: 10.1039/b000000x/

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Figures and tables

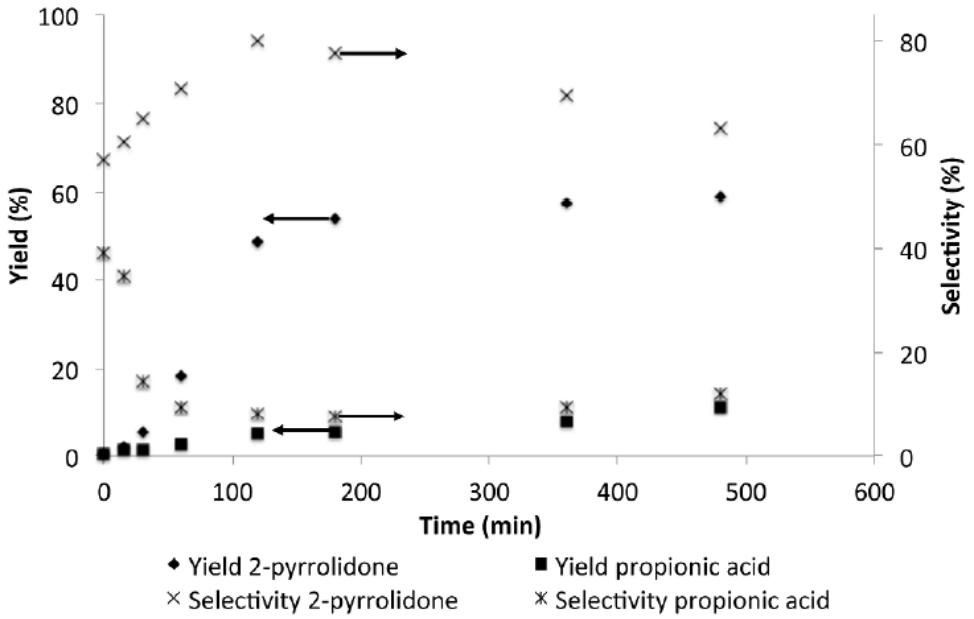
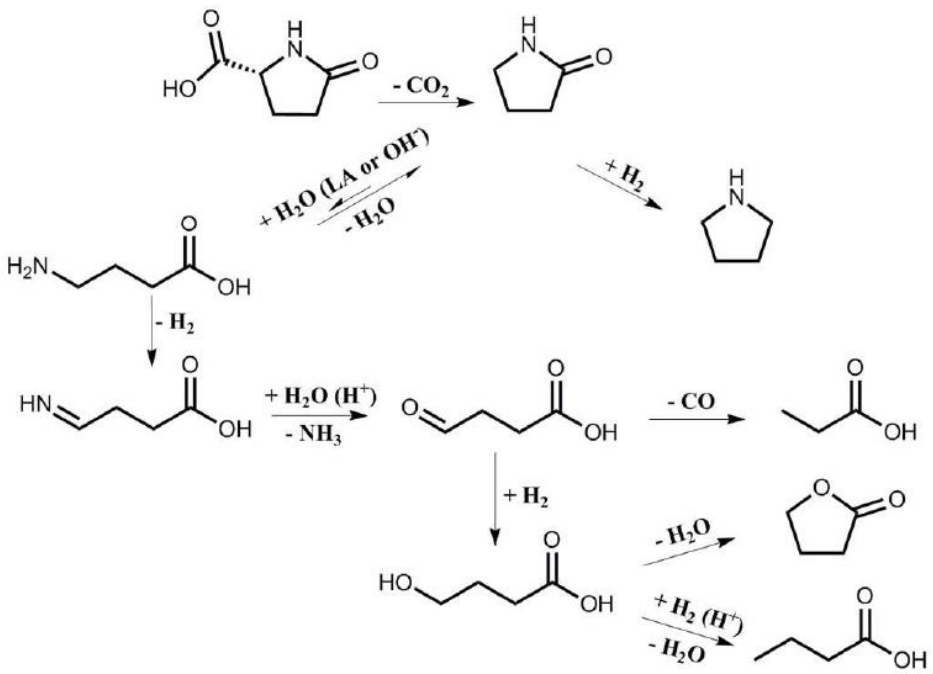


Figure 1. Pd/Al_2O_3 catalyzed decarboxylation of pyroglutamic acid as a function of time. Conditions: pyroglutamic acid (0.2 M in 20 ml water), Pd/Al_2O_3 (2 mol% Pd), 250°C, 6 bar N_2.



Scheme 1. Possible reaction pathways towards the observed side products in the decarboxylation of pyroglutamic acid; acid- or base-catalyzed reactions are marked using brackets; LA: Lewis acid.

Table 1. Catalytic degradation of different lactams by Pd/C catalysts.[a]

Lactam	Main product	Yield (%)
2-Pyrrolidone	Propionic acid	20
δ-Valerolactam	Butyric acid	29
ε-Caprolactam	Pentanoic acid	44

[a]Conditions: lactam (0.2 M in 20 ml water), Pd/C (4 mol% Pd), 250°C, 6 bar N_2, 6 h.

Table 2. Screening of supports for Pd and Pt-based catalysts for the decarboxylation of pyroglutamic acid[a]

Catalyst	Conversion (%)	Selectivity 2-pyrrolidone (%)	Selectivity propionic acid (%)	Selectivity others (%)
Pd/C	82	68	15	17
Pt/C	95	37	32	31
Pd/Al_2O_3	86	81	11	8
Pt/Al_2O_3	85	56	17	27
Pd/ZrO_2	89	65	20	15
Pd/SiO_2	60	81	11	7
$Pd/BaSO_4$	69	72	12	16
$Pd/CaAl_2O_4$	83	69	14	17
$Pd/BaAl_2O_4$	72	70	13	17
$Pd/MgAl_2O4$	99	54	36	10

[a]Conditions: pyroglutamic acid (0.2 M in 20 ml water), catalyst (4 mol% Pd or Pt), 250°C, 6 bar N_2, 6 h. Others: identified C_4-compounds: GBL, GHB, butyric acid and pyrrolidine and non-identified compounds: lower molecular weight compounds.

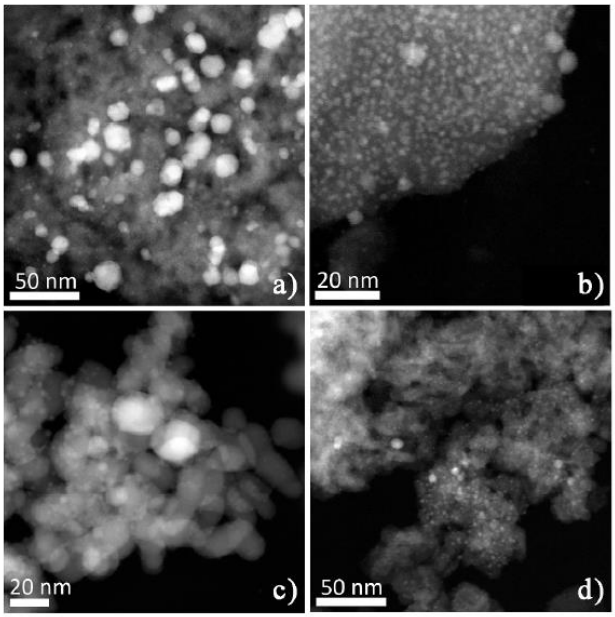


Figure 2. HAADF-STEM pictures of a) Pd/SiO_2, b) $Pd/MgAl_2O_4$, c) Pd/ZrO_2 and d) Pd/Al_2O_3. Pd clusters can be seen as the high-intensity particles in the figure, because of the chemical sensitivity of HAADF-STEM.

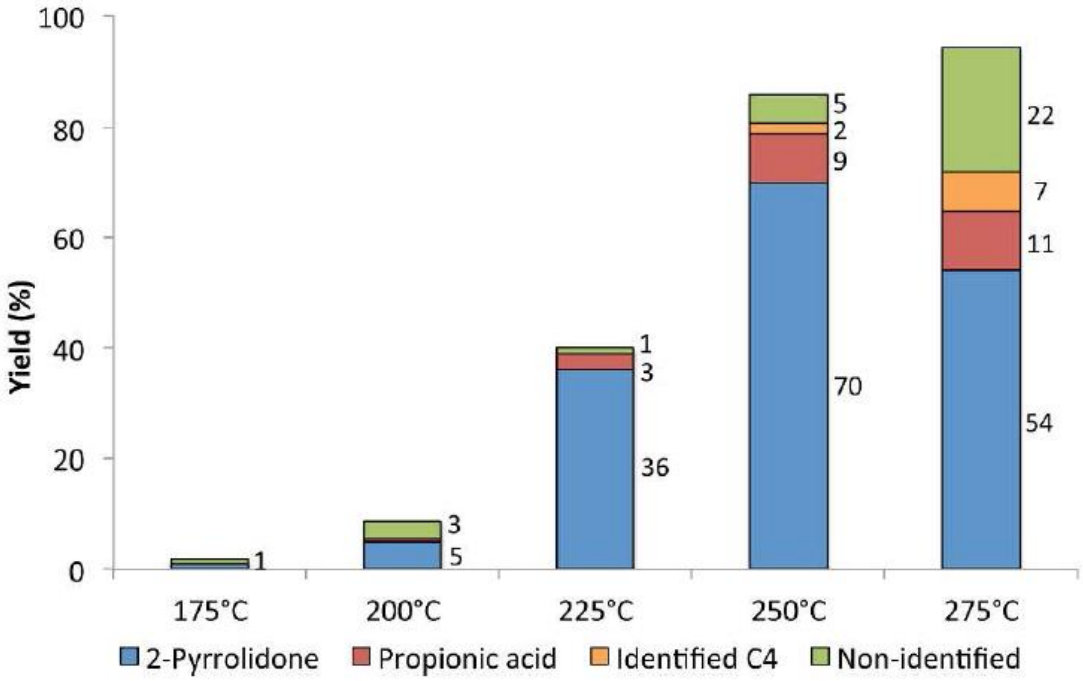


Figure 3. Catalytic decarboxylation of pyroglutamic acid at different temperatures using Pd/Al_2O_3. Identified C_4-compounds: GBL, GHB, butyric acid and pyrrolidine; non-identified compounds are expected to include lower molecular weight compounds. Conditions: pyroglutamic acid (0.2 M in 20 ml water), Pd/Al_2O_3 (4 mol% Pd), 6 bar N_2, 6 h.

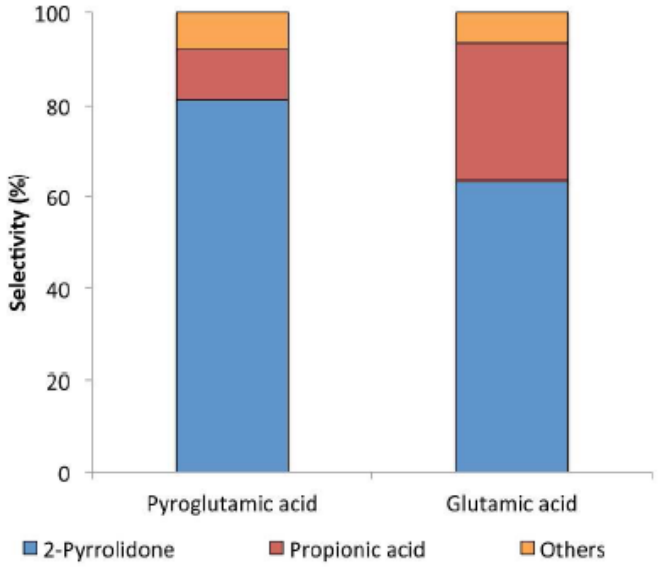


Figure 4. Catalytic decarboxylation of different reactants with Pd/Al_2O_3. Conditions: pyroglutamic acid or glutamic acid (0.2 M in H_2O (20 ml)), Pd/Al_2O_3 (4 mol% Pd), 250°C, 6 bar N_2, 6 h. Conversions: 85% for pyroglutamic acid and > 99% for glutamic acid.

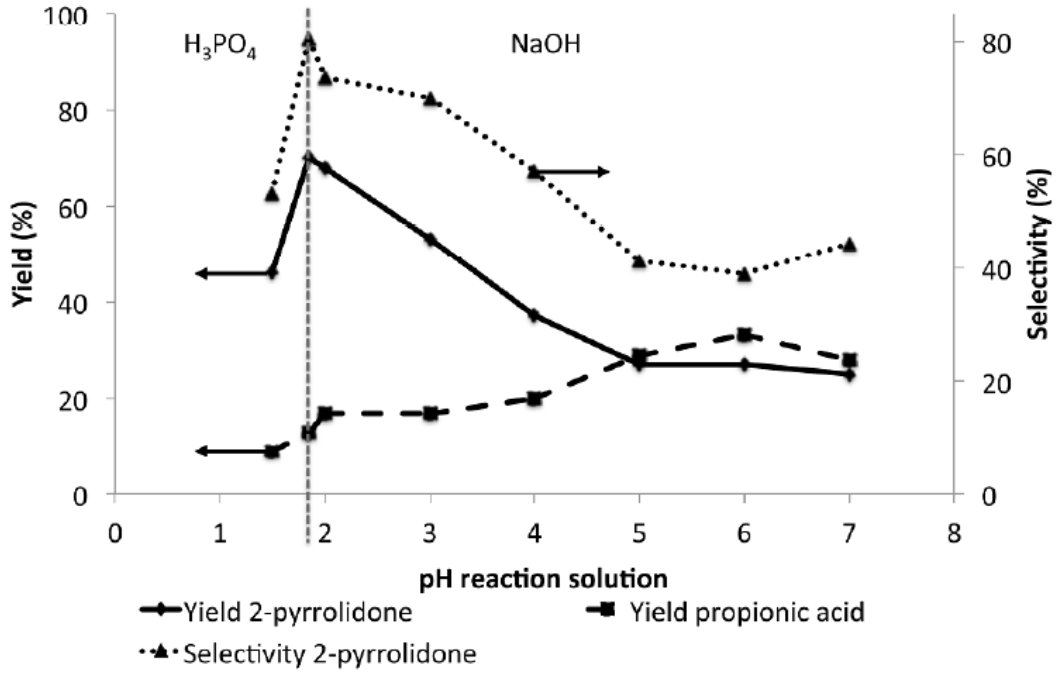


Figure 5. Decarboxylation of pyroglutamic acid at different pH values of the initial reaction solution adjusted with NaOH or H_3PO_4. Conditions: pyroglutamic acid (0.2 M in 20 ml water), Pd/Al_2O_3 (4 mol% Pd), 250°C, 6 bar N_2, 6 h. The dotted vertical line represents a reaction without addition of acid or base.

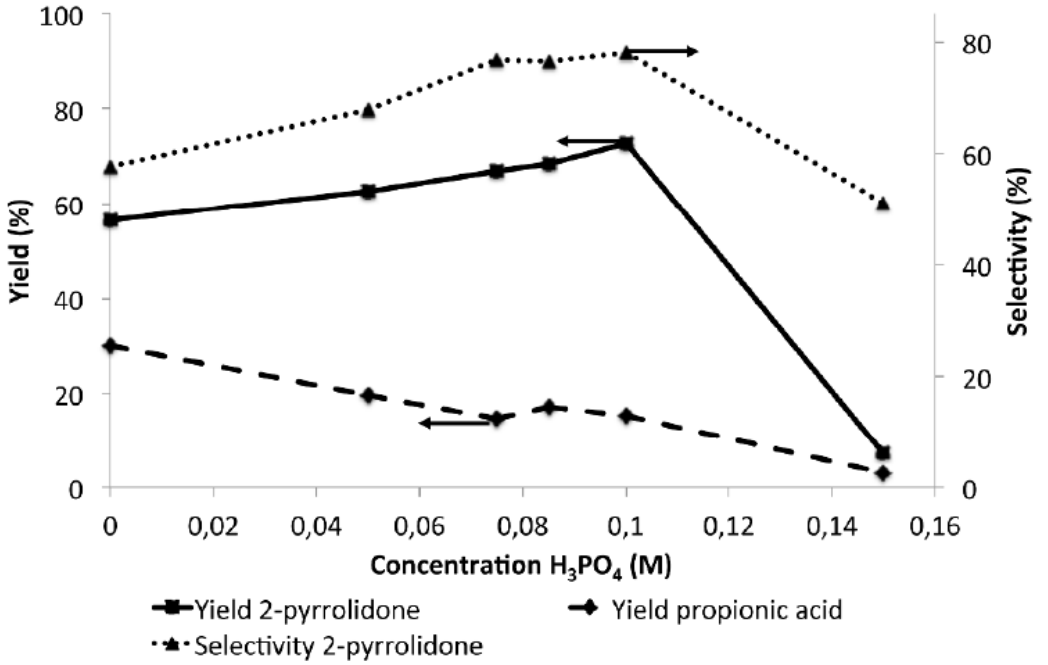


Figure 6. Catalytic decarboxylation of glutamic acid in acidic conditions by adjusting the pH with H_3PO_4. Conditions: pyroglutamic acid (0.2 M in 20 ml water), Pd/Al2O3 (4 mol% Pd), 250°C, 6 bar N_2, 6 h.