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# Unlocking nitrogen-rich biomass-derived amines, amides and nitriles: Mechanisms and (micro)kinetics during catalytic reactions

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ABSTRACT

Nitrogen-rich biomass, the second most abundant biomass after lignocellulosic biomass, holds significant potential for producing N-chemicals. Since such chemicals are predominantly derived from non-renewable sources like fossil fuels, exploring alternative pathways utilizing nitrogen-rich biomass becomes imperative. This review article delves into the utilization of nitrogen-rich biomass, with a particular focus on amino acids, as a raw material for producing N-chemicals. However, it becomes evident that the use of amino acids for fine chemical production through chemo-catalytic conversion still remains relatively underexplored. The key nitrogen-rich biomass sources were reviewed focusing on their potential for N-chemicals production via sustainable chemo–catalytic routes. Amino acids such as glutamic acid and L-lysine resulted as potential raw materials for added-value N-chemicals like amines and lactams. Furthermore, chemo-catalytic conversions towards N-chemicals are discussed. By addressing current challenges and facilitating the in-depth exploration of amino acid conversion, multiscale modelling holds huge potential in advancing sustainable pathways for N-chemical production from nitrogen-rich biomass.

## 1. Introduction

In today's conventional oil refineries, most fuels and chemical feedstocks are produced from non-renewable sources such as crude oil, coal, or natural gas [1]. This is associated with numerous environmental problems, such as $CO_2$ pollution and availability issues [1]. It is therefore necessary to reduce our dependence on fossil sources and switch to renewable and sustainable sources such as biomass [2]. Biomass, as a widely available and cost-effective renewable source, is mainly associated with lignocellulosic (LC) biomass, composed of cellulose, hemicellulose, and lignin, whose annual production is estimated at 170 billion tons [3]. Furthermore, due to its composition, lignocellulosic biomass can only be directly converted into compounds containing C, H, or O elements, so-called O-chemicals, leaving behind some valuable chemicals containing a nitrogen element that could also benefit from the biomass [1]. Chemicals with the nitrogen element in the structure, known as N-chemicals include nitriles, amides, amines, and many others with a wide range of applications such as medicine, textiles, pharmaceutical compounds, etc. [3]. Amines are particularly important and widely used as their use is closely related to the production of polymer materials, especially polyamides [4].

The increasing number of studies on the conversion of lignocellulosic biomass over the last decade have led to increasing amounts of bio-based fuels and chemicals [3,4]. Furthermore, these final products of lignocellulosic biomass conversion (see Fig. 1) lead to a massive availability of useful compounds that can either be used directly as O-chemicals or upgraded to N-containing products, which offers several advantages [3,4]. N-chemicals are economically more valuable compared to O-chemicals [3,4]. Additionally, increasing LC valorisation results in more sustainable raw materials available for the conversion in N-chemicals [3,4]. Besides many advantages of the conversion of O-chemicals into N-chemicals, the major drawback is related to the use of ammonia ($NH_3$) to incorporate nitrogen into the structure [4]. The use of ammonia in amination (see Fig. 1) adds complexity to the process, even if the implementation of compounds from LC valorisation saves the additional steps at the beginning [5]. From an economic and sustainability point of view, it is more practical and easier to obtain such N-chemicals directly by the so-called one-pot process from nitrogen-rich biomass [4]. Nitrogen-rich biomass (see Fig. 1) is one of the attractive and widely available biomasses covering all the crucial elements described above

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and consisting of algae (e.g., microalgae) [6–9], crustaceans (e.g., shrimp) [10] or industrial or agricultural waste (e.g., residues from seafood production or bioethanol production from wheat straw or corn stover) [8,11]. In addition, biorefinery strategies for N-chemicals could lead to better economics and lower environmental impact in the production of such bulk chemicals than the corresponding petrochemicals due to their availability in nature [11,12].

This review article summarizes the current status of potential nitrogen-rich biomasses that can be converted into high-value-added N-chemicals. However, only the step from pure compounds to value-added N-chemicals was considered, not considering the whole process from biomass to high-value-added N-chemicals due to finding a significant gap in the current state-of-the-art research. Therefore, the availability of biomass via potential N-chemicals and recent studies on the chemocatalytic conversion of such components are presented. In silico studies and multiscale modelling are presented as descriptive and predictive tools for the conversion of nitrogen-rich biomass into value-added N-chemicals. Finally, upscaling such transformations requires a comprehensive knowledge of the lower-level processes to reach the higher level with more complex mathematical simulations and computations, which is significantly lacking in current research and represents an important opportunity for further investigation.

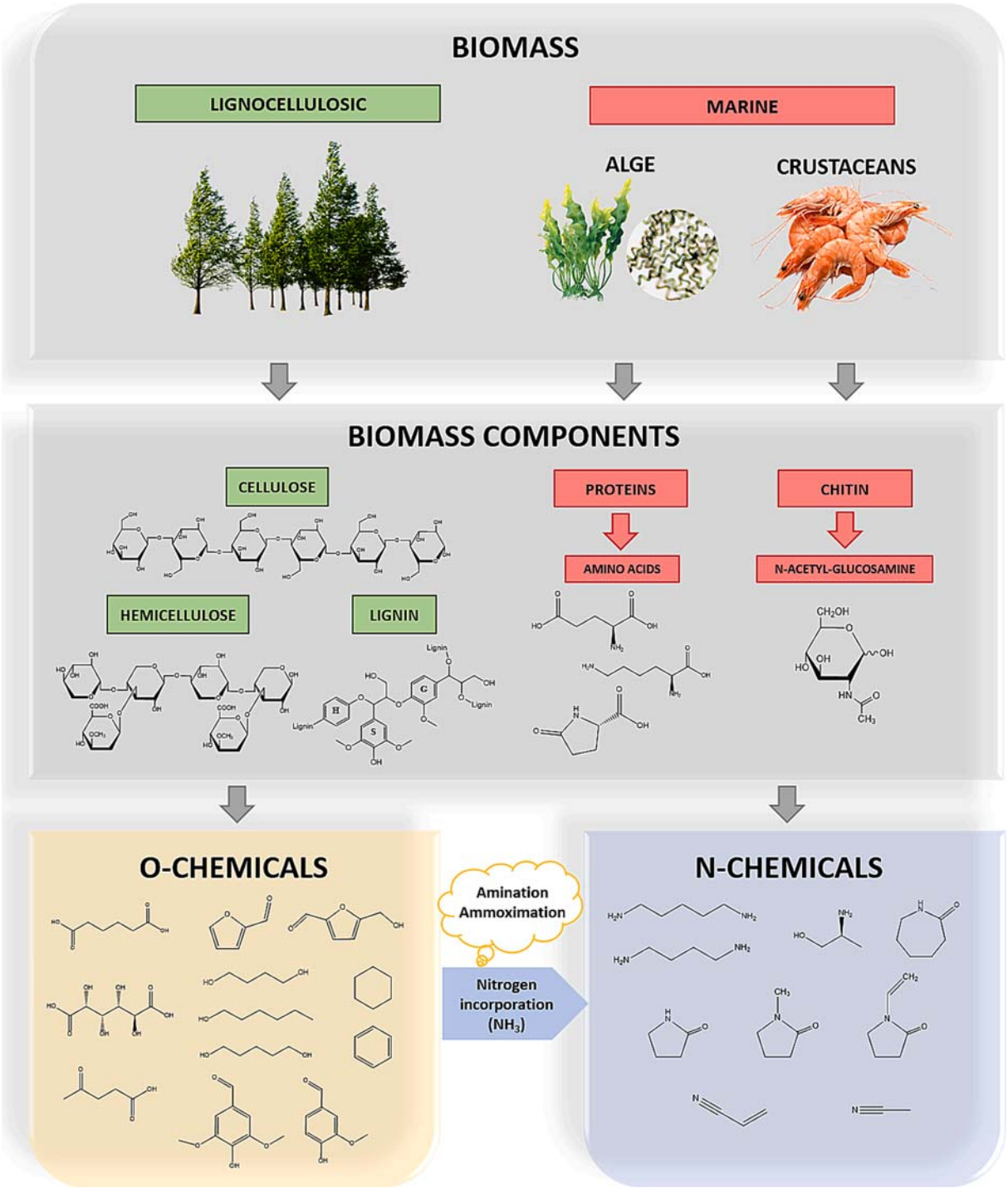


**Fig. 1.** Lignocellulosic and marine biomass to high-value O- and N-chemicals.

## 2. Nitrogen-rich biomass for the sustainable production of N-chemicals

The following sections comprehensively describe the current availability and production of nitrogen-rich biomass, with a particular focus on algae—one of the largest segments by weight among all nitrogen-rich biomasses. By definition, algae are photosynthetic and aquatic organisms found in either fresh or seawater such as oceans, rivers, etc. [13]. This biomass presents a valuable biomass that can produce proteins, lipids, polysaccharides, and other components, when sufficient supply of $CO_2$, water, oxygen, and essential nutrients (e.g., potassium, phosphorus, etc.) is available [13,14]. Notably, global algae production is increasing with the production in 2019 being 35.82 million tons [15]. The largest producer is Asia, which accounts for 97 % of total annual global production [15]. Among Asian countries, China holds the highest production capacity, contributing 57 % of the annual global output [15]. Other major Asia-based producers are Indonesia (27 %), Republic of Korea (5 %), and Philippines (4 %) [15–17]. As global production of algae grows, its applications are exponentially expanding across industries.

Interestingly, algae have numerous commercial applications, but in Asia, algae are primarily used as food, which is not so common in other parts of the world [13,18]. However, in recent years, they have started to be used in food and other applications outside Asia [18]. In particular, in Europe, for example, some algae are extensively used for antioxidants and vitamins production or are used directly as feed or fertilizer in agriculture [18]. A notable example of this shift is seen in a comprehensive study of the European algae production industry conducted in 2021 report that 225 companies produce either macroalgae (67 %) or microalgae (33 %) (see Fig. 2), with numerous companies producing *Spirulina* species as microalgae [18]. As a result of the frequently mentioned global and local availability and the growing market of the algae segment, new applications such as biofuels, biopolymer materials, and high-value-added chemicals for algae use have started to emerge [13,18–20]. Consequently, as noted, the growing global market for algae, specifically microalgae, one of the subgroups of algae group, makes microalgae extremely interesting for various applications, of which the availability, composition and cultivation needs to be discussed.

### 2.1. Microalgae

#### 2.1.1. Availability of the microalgae biomass

The global market value of microalgae (see Fig. 2) was estimated at 11.8 billion USD in 2023 and is forecast to reach 25.4 billion USD by 2033. In fact, the annual growth rate between 2023 and 2033, (CAGR) was calculated to be 8 % [21]. Based on this growth, it is clear that the development of sustainable technologies for microalgae utilization as feedstock for the production of bio-based compounds will further increase market value and ultimately steer society towards a circular economy in which microalgae consume $CO_2$ to produce value-added compounds that are then further used for the production of drop-in chemicals [14]. As presented, their growth in the market makes them interesting for more applications.

The role of microalgae in the production of bulk platform chemicals is becoming increasingly attractive due to numerous advantages, such as $CO_2$ consumption leading to a reduction in greenhouse gasses (GHGs) emissions and highly efficient production in terms of capacity and harvesting [14]. Microalgae can be easily harvested within 1 – 10 days (depending on culture size and technology), which contributes significantly to availability and could potentially lead to a lower price of the raw materials [7]. Moreover, their growth rate is 5 to 10 times faster compared to other crops such as wheat or maize, which means that they can produce large amounts of available biomass that cannot be achieved with conventional agricultural technologies [22,23]. As a result, microalgae are rapidly gaining attention due to their advantages and composition as a sustainable resource for the production of valuable high-value products.

Microalgae (see Fig. 2), as small autotrophic unicellular organisms, are by definition composed of both eukaryotic and prokaryotic organisms [14,21,23]. Their composition is similar to that of algae, with the main components being lipids, proteins, polysaccharides, and some residues (e.g. antioxidants), with lipids known to be mainly used for the production of biofuels [14,22]. Biofuels produced from microalgae are considered a third-generation biorefinery and are a feasible alternative to partially or completely replace fossil fuels [5,8,22]. The use of biofuels has several advantages, such as direct blending with existing fuels, higher sustainability and energy content [5,8,22]. Microalgae are the richest protein source on Earth as nitrogen-rich biomass [5,11].

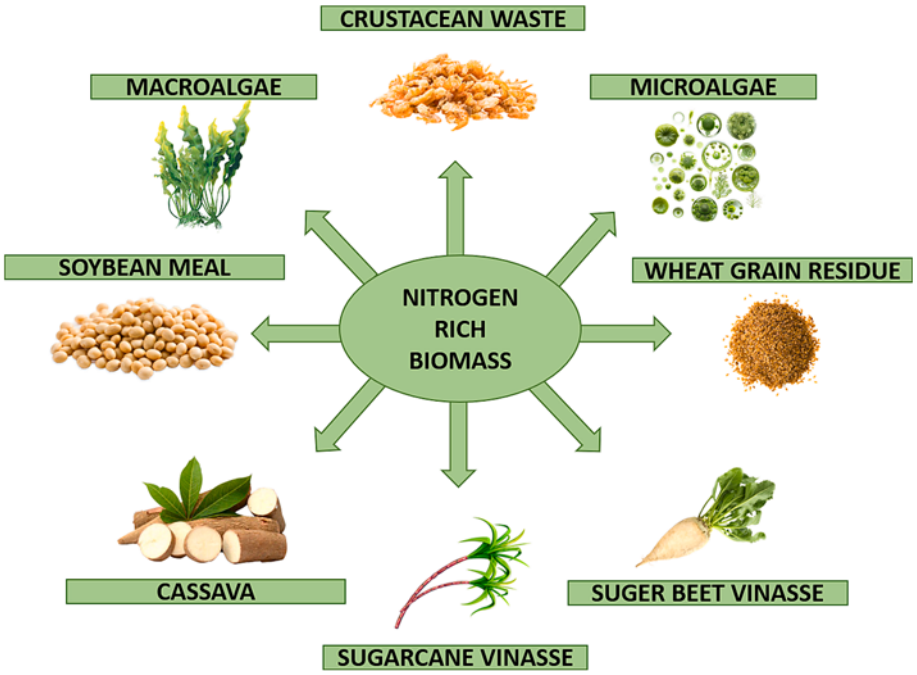


**Fig. 2.** All the potential nitrogen-rich biomasses.

Therefore, it is obvious that it is interesting and more attractive from a sustainability perspective to fully utilize microalgae (see Fig. 2) in the conversion of existing compounds (e.g., proteins) into fine N-chemicals [5]. This underscores the need to explore their composition and cultivation techniques, as these factors are essential for optimizing microalgae for further high-value applications such as N-chemical production.

#### 2.1.2. Microalgae composition and cultivation

Microalgae organisms are incredibly versatile and adaptable, as they can be cultivated in different waters (e.g., oceans or rivers) and can tolerate a wide range of pH values [14]. Because of their extreme adaptability, they are suitable for cultivation in areas that do not compete directly with agricultural land [22,23]. Currently, it is estimated that there are 200,000 known species of microalgae, some of which are recognized as food-safe, such as *Chlorella*, *Dunaliella,* and *Spirulina* [23]. However, there are many more that are still unknown [23]. In general, the protein content of microalgae is between 30 wt %-80 wt%, depending primarily on the species used [23]. For example, protein content of 31 to 46 wt% is found in *T.chuii*, while an average of 51 wt% to 58 wt% of proteins is found in *Chlorella vulgaris* and the highest content of 50 wt%-80 wt% can be found in *Dunaliella salina* [23]. The large-scale production of microalgae began in the 1960 s, with *Spirulina* being the first species [22]. Globally and locally (e.g., in Europe), dominant species by weight are *Chlorella* and *Spirulina* (*Arthrospira*), which generally contain 50 wt%-60 wt% dry weight of proteins [11,15,17,23]. As a result, these species are widely cultivated in different methods for various applications presented earlier.

To achieve this large-scale production, there are two cultivation techniques for microalgae; open and closed culture systems [15,17]. The oldest and simplest technique is open pond cultivation, where species *Spirulina* and *Chlorella* are most commonly produced [22]. This method offers numerous advantages, such as easy maintenance and scalability, higher production capacity and energy efficiency [18,22]. However, the major disadvantages of the open pond system are the homogenization of nutrients and lack of process conditions control [18,22]. On the other hand, closed cultivation systems are commonly associated with the photobioreactors (PBR) available in different designs from tubular to a flat plate, producing mainly one microalgae species [22]. Such a method possess high production capacity in more compact production facilities, offering more controlled reaction conditions (e.g., mixing, temperature, etc.) [24]. The major disadvantages of closed systems are the higher operating costs and potential cell damage or overheating of the system [18,24]. In the EU, 71 % of the production of microalgae is done in photobioreactors (PBR), around 19 % in ponds and around 10 % in fermenters [18]. While both open and closed cultivation systems have their respective advantages and disadvantages, it is important to remember that despite their efficient production, these systems can lead to environmental problems that must be addressed. These include high resource consumption and pollution potential, which must be considered [14,18].

The production of microalgae benefits the environment, as discussed earlier, due to providing a renewable source for the production of biofuels by reducing $CO_2$ emissions [14]. However, it also comes with challenges that can potentially impact the environment, such as high water and energy consumption, pollution other than $CO_2$ emissions, and the risk of microbiological contamination [14,18]. However, microbiological contamination, in our opinion, is considered a general problem in biotechnologies [14,18]. Specifically, it was found as a major problem in the past, e.g., contamination of ecosystems where such microorganisms do not naturally occur [14,18]. Additionally, the intensive use of water and energy resources required for large-scale production could pressure local ecosystems, which would be particularly problematic in areas with water shortages or energy limitations [14,18]. Moreover, its production process could also lead to emissions of other pollutants (e.g., input materials, by-products) if their production is not adequately managed or optimized [14,18]. Considering the challenges associated with the production of microalgae, it is important to note that as technologies mature, these issues could be reduced. However, at the same time it is equally important to explore the potential of macroalgae/seaweeds for the production of N-chemicals due to distinct advantages in terms of availability, composition, and cultivation, making them a viable biomass for the production of N-chemicals.

### 2.2. Macroalgae

#### 2.2.1. Availability of the macroalgae biomass

The second largest segment of the algae sector are macroalgae (see Fig. 2) which generally contain less proteins than microalgae, however, their use would no significantly impact the food production and are, therefore, suitable as a raw material for the production of bulk chemicals [11,15,25]. Their market size was 9,302.6 million USD in 2023, and is expected to reach 18,305.1 million USD by 2033, with a CAGR of 7.8 % [26]. In fact, their main area of application area is still the food sector, as supplements, preservatives, and thickeners [17]. Nevertheless, their use is expanding to other areas, such as cosmetics, (bio)fertilizers, animal feeds, alginate and agar production, bio-packaging, biofuels, and pharmaceutical compounds [8,11,15–17]. Given their expansion in the applications and growing market, it is crucial to study their composition and cultivation methods to understand better their potential for their use as sustainable resources of components for the production of N-chemicals.

#### 2.2.2. Macroalgae composition and cultivation

Macroalgae or seaweed are eukaryotic multicellular marine organisms which, unlike microalgae, are visible to the naked eye [8,16,17]. Their composition is like microalgae, with main components, being lipids, proteins, polysaccharides, and some residues but being richer in vitamins and minerals [15,23]. In fact, they are divided into three groups, namely brown seaweeds with around 2,000 species, red seaweeds with more than 7,200 species, and green seaweeds with over 1,800 species [17]. Furthermore, in 2019, Asia had 97.4 % of global seaweed production, with China being the largest producer [17]. As a result, brown seaweeds are the most widely produced seaweeds reaching 16 million tons in 2019 [17]. Among them, *Laminaria [Saccharina] japonica* is the most widely produced macroalgae, accounting for 35.4 % of total global production, with 12.3 million tons produced worldwide [17]. Generally, the protein content of macroalgae is between 8 wt%-40 wt% averaging at 20 wt% [11]. Notably, the highest protein content is found in the red seaweed *Porphyra,* with a protein content of over 40 wt % [11]. On the other hand, a protein content of only 15 wt%-20 wt% can be found in red seaweed known as *Gracilaria* and the lowest protein content is found in the brown seaweed *Laminaria* with a content of 8 wt %-15 wt% [11]. This provides the basis for understanding the various harvesting and cultivation techniques, which will be further analysed in more detail, considering both wild harvesting and cultivation techniques.

For the production of macroalgae/seaweeds, two technologies are used worldwide and locally in Europe, namely wild harvesting and agricultural harvesting (cultivation) [15,18]. Wild harvesting, which is mainly used in Europe, is further subdivided into manual and mechanical harvesting, both of which are time-consuming [15,18]. Mechanical harvesting (only 15 %) uses a fleet of specialized vessels, while the vast majority (85 %) is still harvested by hand [15,18]. While wild harvesting, as presented, remains a prevalent method in Europe for macroalgae production, the increasing focus on agricultural harvesting techniques, such as land-based and coastal cultivation, offers a more sustainable and efficient alternative that addresses the challenges associated with time-consuming wild harvesting.

Interestingly, on the global scale microalgae production in 2019 was largely based on agriculture methods rather than wild harvesting [17]. Agricultural production of microalgae/seaweeds is seen as a way to meet the demand for macroalgae/seaweeds biomass on the market. Some

European countries, such as France, Spain, and Portugal, have already found the commercial scale with two agricultural techniques, one implemented on land and the other conducted along the coast [15,18]. While, land-based technologies require a significant amount of land area and their operational costs are high due to the equipment and infrastructure needed [18]. Therefore, such productions mostly target high-value products, e.g. functional chemicals or pharmaceutical compounds [18]. In general, this production offers more control over the biomass produced in terms of quality and composition [18]. Conversely, cultivation at sea offers lower operating costs and better scalability than on land but also has some disadvantages, mainly related to the lower control of the process, resulting in lower yields, risk of diseases, and environmental controls [18]. Most of these cultivation areas are located in shallow oceans and coastal areas highlighting the trade-offs involved in choosing between these two methods [18].

Further, a comparison between macroalgae and microalgae finds a higher potential for microalgae for the direct conversion to N-chemicals due to their more straightforward structure, but as mentioned, the direct conversion to N-chemicals is not the subject of this review. Although macroalgae possess a lower protein content with a more complex structure, as mentioned, they compensate for this with greater availability and easier but more time-consuming cultivation, e.g., through wild harvesting, whereas their direct utilization would require more steps to produce final N-chemicals.

While global macroalgae production relies on agricultural cultivation to meet market demands, exploring other nitrogen-rich biomasses, such as agricultural waste [11], also presents the potential for producing valuable N-chemicals.

### 2.3. Other nitrogen-rich biomasses

Besides microalgae and macroalgae, there are also several other natural resources rich in nitrogen-rich compounds, especially crustacean shells and other agricultural wastes [4,11]. In particular, agricultural wastes that represent another protein-rich biomass include corn and wheat grain residues (see Fig. 2), which contain an average of 27 wt% of proteins [11]. Additionally, sugar cane and sugar beet by-products also have the potential to be used as nitrogen-rich biomass [11]. The sugarcane by-product is sugarcane vinasse (see Fig. 2), which is a by-product of bioethanol production and has an average protein content of 13 wt% [11]. Similarly, the by-product of sugar beet is beet vinasse with a protein content of 33 wt% [11]. Cassava (see Fig. 2), another by-product of bioethanol production, has a protein content of 35 wt% and could present a potential source of N-chemicals [11]. Moreover, by far, the most interesting N-containing feedstock is from natural (vegetable) oil production or biodiesel production [11]. Vegetable oil production focuses mainly on soybeans, palms, or sunflowers, from which large quantities of oil meal are produced and could be used as feedstock [11]. Notably, globally, the largest is soybean meal production (see Fig. 2), which contains 50 wt% of proteins to be further utilized for conversions to value-added N-chemicals [11]. The wide range of agricultural wastes that can be utilized for sustainable production of N-chemicals, additionally, crustacean shells [4], represent another valuable nitrogen-rich resource with significant potential for conversion into N-chemicals.

Marine biomass and seafood wastes like crustacean shells (e.g., carbs, shrimps, etc.) (see Fig. 2) not only contain a high content of proteins (20 %-40 %), but they also contain chitin as their main component (15 %-40 %), which can be used for the production of high-value N-containing products or chemicals [1,4,27]. Globally, 6–8 million tons of crustacean shell waste are generated every year [1,27]. Due to their high availability, the development of a shell biorefinery concept in 2015 aimed to convert chitin into N-chemicals and other added-value materials [1,4]. This concept is feasible because of the vast amounts of chitin produced [1,4]. In fact, annual production in 2021 was around 100 billion tons, making it the second largest naturally occurring compound [4]. However, as with any new technology, there are some limitations to its use, such as the high molecular weight and crystallinity of chitin [1]. In polymer chemistry, chitin is a linear polymer consisting of monomeric units called *N*-acetyl glucosamine linked via β-(1,4), with a chemical structure similar to that of cellulose, but with nitrogen fixed in the form of an amide functional group [1,4]. Over the years, various chemical approaches have been developed using chitin as a raw material, resulting in the main products being amino sugars or alcohols, amide sugars, or other N-chemicals [1].

Given that high protein content was found in all the discussed nitrogen-rich biomasses, it is important to investigate the potential of this proteins or their monomers, known as amino acids, derived from these sources for the production of N-chemicals and other functional materials.

### 2.4. Utilizing proteins: Enhancing potential biomass value-added components

Microalgae, macroalgae or seaweeds, and other nitrogen-rich biomass (e.g., agricultural waste) are all generally composed of proteins with different contents. According to Lammens *et al.* [11], in the review from 2012, calculated that microalgae would provide 300 million tons of proteins annually that could be used for the production of high-value N-chemicals, while macroalgae/seaweeds would only provide 3 million tons. However, due to the growing market demand, increased availability of biomass, and a wide range of new applications for proteins, these figures have significantly increased in recent years [11]. The valorisation of these proteins from biomass to commercial-scale applications can be achieved through various methods including chemical, enzymatic or microbiological approaches [2]. As a known nitrogen source, proteins consist of 20 different amino acids with more than 50 amino acids linked together in a specific order to form a complex polymer [2,11,28–30]. Each amino acid functions as a monomer with carboxylic and amine groups, some of them even contain sulfur, which provides them with suitable functionality and reactivity for producing numerous platform chemicals [2,31]. In particular, two amino acids, L-lysine and glutamic acid, are interesting to be discussed in respect to their availability and commercial production methods, which is critical for maximizing their potential for conversion to value-added N-chemicals [2,11,31,32].

Notably, glutamic acid is one of the most abundant amino acids, with a high content in proteins in the most common micro- and macroalgae species, which makes it particularly promising for conversion into bulk chemicals [2,11,31–34]. In fact, the global glutamic acid market size was 13.31 billion USD in 2023, growing at a CAGR of 5.9 % between 2023–2032 [35]. Furthermore, the annual production of glutamic acid was estimated at 2.8 million tons in 2023, with the most common production technique being bacterial production via fermentation using *Corynebacterium glutamicum* and sugars as raw material (e.g. glucose) to minimize production costs [31,36–38].

Lysine is the second most important amino, boasting huge potential for use as a raw material in bulk chemicals production, with a global market value of 8.44 billion USD in 2022 and a CAGR of 7.5 % between 2023 and 2029 [2,31,39]. Its commercial production is primarily based on bacterial fermentation of sugars (e.g., glucose and fructose) using *Corynebacterium glutamicum*, resulting in an annual production of 3 million tons in 2022 [40–43]. Despite the progress, both amino acids are not yet produced from biomass or agricultural waste, however, research is actively exploring how these amino acids can be derived from alternative feedstocks [36,37]. This process primarily involves producing a mixture of amino acids via hydrolysis of proteins derived from nitrogen-rich biomass, which poses significant separation challenges [2]. In fact, amino acids can be separated based on hydrophobicity, size, solubilization, or electrochemical characteristics and are, therefore, categorized as acidic, basic, or neutral [2]. Techniques like electrodialysis with an ion exchange membrane can be employed for separation, though arginine separation may require a special membrane [2,11]. Other methods

include modifying amino acids to make them more easily separable [2].

Based on the discussion of lysine and glutamic acid derived from nitrogen-rich biomass such as algae, these amino acids offer significant potential as feedstocks for the production of valuable N-chemicals, including diamines, lactams, amino alcohols and nitriles. One of the advantages of such an approach is that these N-chemicals can be obtained directly from the above-mentioned amino acids. The question arises as to whether the production of these compounds is worthwhile, emphasising the need to investigate their economic feasibility. The advantage of such an approach is that these N-chemicals can be obtained directly from the above-mentioned amino acids by innovative methods.

## 3. Promising bio-based nitrogen-containing chemicals

The following section considers important N-chemicals, focusing on their applications, market size, annual production capacity, existing production methods, bio-based alternatives, and biotransformation methods. Two main selection criteria were used for the selection of the described N-chemicals:

I. The potential of directly obtaining these N-chemicals from amino acids with minimal conversion steps. For instance, products with the same or fewer carbon atoms are considered if an amino acid has six carbons.
II. The applications of the selected N-chemicals, which are mostly used in the polymer industry.

Based on these above-mentioned criteria, N-chemicals such as diamines like cadaverine (1,5-diaminopentane) and putrescine (1,4-diaminobutane); lactams such as ε-caprolactam and 2-pyrrolidone and its derivatives; and amino alcohols and nitriles, including acrylonitrile and acetonitrile were selected to be discussed in their economic feasibility.

### 3.1. Amines

Amines and bio-based diamines, used in applications such as polyamides and polyurethanes, have significant potential as biomass-derived N-chemicals, in contrast to their petrochemical production routes, which rely on ammonia [44]. In this context, the search for alternative, economical and environmentally friendly production methods using compounds that are functionally similar to (di)amines is becoming increasingly attractive, with protein-derived amino acids showing great potential [31,45]. In particular, L-lysine, glutamic acid, and other amino acids can serve as important raw precursors for direct conversion into the two widely used diamines, specifically cadaverine/1,5-diaminopetane and putrescine/1,4-diaminobutane, and are discussed in the following section with regard to potential to be produced via alternative production routes [31,44,45].

#### 3.1.1. Cadaverine/1,5-diaminopetane

Cadaverine, also known as 1,5-diaminopentane, 1,5-pentanediamine or pentamethylene diamine, is a colourless, viscous liquid with an irritating odor, used as a platform N-chemical and building block in applications such as polyamides, polyurethanes, additives, and sequestering agents [46,47]. As a high-performance material, polyamides had a global market size of 35.6 billion USD in 2022, expected to grow to 54.9 billion USD by 2032 [48,49]. Additionally, cadaverine is a linear aliphatic diamine from the polyamine group, which was first identified in human cadavers, giving it its name [46]. However, the petrochemical production route has drawbacks, including equipment corrosion, low selectivity, catalyst stability issues, and challenges in achieving stable, continuous production [47]. Consequently, due to the increasing global polyamide market, new bio-based production methods need to be developed to replace traditional petrochemical processes to improve sustainability, and support a circular economy. Therefore, the global market, and current petrochemical and biochemical production processes need to be discussed to fully assess its potential.

The global market size for cadaverine was 42 million USD in 2023, with predictions for further growth [50]. Developing bio-routes aims to replace petrochemical methods, enhancing eco-efficiency and supporting a circular economy for greater sustainability [46]. In this regard, biocatalysis offers improved selectivity and a shift from fossil to renewable sources [46,47,51]. Currently, bio-based cadaverine is produced using whole-cell bioconversion or fermentation, utilizing lysine decarboxylase or microorganisms like *Corynebacterium glutamicum* [44,46,51]. Industrial-scale production already occurs at companies like Cathay Industrial Biotech (Shanghai, China), Ningxia EPPEN Biotech (Ningxia, China), and Ajinomoto (Tokyo, Japan) [44]. However, challenges remain, including enzyme efficiency and stability, cadaverine purification, wastewater treatment, and high costs of additives [46]. Cadaverine produced via alternative routes could be used for bio-polyamide synthesis, with the second monomer derived from sustainable sources like lignocellulosic biomass [46]. Examples include succinate, sebacic acid [46] or, recently, adipic acid [52]. New, more economical, and efficient technologies are needed, with chemo-catalytic conversion of L-lysine offering potential for higher reaction efficiency and renewable feedstock utilization [47].

In addition to cadaverine, putrescine (1,4-diaminobutane) comes to mind as another important diamine with wide applications in the industry, particularly as a platform chemical for the production of polyamides [31].

#### 3.1.2. Putrescine/1,4-diaminobutane

Putrescine, chemically known as 1,4-diaminobutane, is the second most common diamine and has significant potential for production via alternative routes, which is utilized in various applications, including polymer materials (e.g., as a comonomer with adipic acid to produce nylon 4,6), surfactants, pharmaceuticals, and agricultural chemicals [31,44,51]. The global market size was 126.4 million USD in 2021 [53], with an annual demand of around 10,000 tons [44] and market prices ranging from 1000 to 3000 USD per ton [54]. Currently, the preferred petrochemical route for producing 1,4-diaminobutane involves using propylene, ammonia, and hydrocyanic acid [31]. However, sustainable alternatives could involve the use of amino acids like L-arginine, serine, L-glutamic acid, or L-ornithine, using biotransformation with enzymes or microorganisms such as *Corynebacterium glutamicum,* similar to cadaverine production [31,44,51].

Following the discussed diamines, lactams also represent the big class of N-chemicals, which still lack the sustainable production that can also be used in the polymer industry, e.g., polyamides [55].

### 3.2. Lactams

Lactams are highly demanded N-chemicals with strong potential to be produced via more sustainable methods instead of petrochemical resources. This review focuses on ε-caprolactam and 2-pyrrolidone or their derivatives, as these compounds can be directly converted from amino acids such as L-lysine and glutamic acid, respectively. The emphasis on these compounds is also related to the fact that they are the final products of the chemo-catalytic conversion of L-lysine and glutamic acid, discussed in the later section on the chemo-catalytic conversion of amino acids.

#### 3.2.1. ε-Caprolactam

ε-Caprolactam, primarily used as a monomer for producing polyamide 6 in the polymer industry, had a global market value of 15 billion USD in 2022, with annual production reaching 8.824 million tons, predominantly in Asia [55–57]. The market price for ε-caprolactam is around 1650 USD per ton [58]. Companies such as Advansix Inc., The Aquafil Group, and BASF SE rely heavily on petrochemical routes using fossil fuels as feedstocks [57]. Industrial production, which began in 1943 initially used phenol as a raw material, converting it to

cyclohexanone and then to cyclohexanone oxime before obtaining ε-caprolactam [55]. In the 1990 s, SINOPEC introduced a more sustainable process using benzene to synthesize cyclohexanone oxime before ε-caprolactam [55]. Today, approximately 90 % of ε-caprolactam is produced via the cyclohexanone pathway, while the remaining 10 % uses nitrosyl chloride and cyclohexane in the Beckmann rearrangement [59].

To reduce reliance on fossil fuels and address environmental concerns, developing more sustainable and economical bio-based production routes for ε-caprolactam is essential [59]. L-lysine's similar structure, low cost, and availability makes it a promising bio-based feedstock. Emerging technologies are focusing on using biomass components, such as L-lysine, through homogeneous and more sustainable heterogeneous catalysis [55,59–61]. Building on the chemistry of ε-caprolactam, 2-pyrrolidone emerges as another important lactam to be discussed in the following section with a wide range of applications and the potential to be directly converted from glutamic acids, which will be the focus of the later section on chemo-catalytic conversion of amino acids.

#### 3.2.2. 2-pyrrolidone and its derivates

The second most prominent lactams, 2-pyrrolidone and its derivatives (N-vinyl-2-pyrrolidone and N-methyl-2-pyrrolidone), hold significant potential for sustainable production due to their wide range of industrial and commercial applications [62,63]. These compounds are commonly used as industrial solvents, plasticizers in aqueous coatings, curing accelerators in acrylic emulsions, and copolymers in acrylic/styrene floor polishes [64]. Additionally, they serve as precursors for polyvinylpyrrolidone, surfactants, pharmaceuticals, and agricultural chemicals [62,64,65]. In 2022, the global market size for 2-pyrrolidine was 350.19 million USD [66] with a market price of 2900 USD per ton [67]. Its derivatives also show substantial market presence, with N-vinyl-2-pyrrolidone and N-methyl-2-pyrrolidone, having a market size of 2663.04 million USD (in 2018) [68], and 956.7 million USD (in 2022) [69], respectively. Production of N-vinyl-2-pyrrolidone reached 80,563 tons in 2023 [70] and for N-methyl-2-pyrrolidone reached 650,000 tons in 2023 with a price between the 2000 to 2800 USD per ton [71,72].

Conventional production of pyrrolidones involves a two-step reaction with alkyl amines and lactones, followed by hydrogenation using Pd or Rh catalysts on carbon at 100 °C and 55 bars of hydrogen [63,73]. However, this process heavily relies on fossil-based α-angelica lactone and consumes significant amounts of hydrogen [63,73,74]. Conventional pyrrolidones also pose health risks, including respiratory irritation and other effects, and are classified as hazardous under REACH [63]. In contrast, N-substituted-5-methyl-2-pyrrolidones (5MP) offers a safer alternative, as they are not classified as hazardous and are already used in similar applications, including solvents, surfactants, pharmaceuticals, and agricultural chemicals [63,73].

Therefore, there is growing interest of producing both conventional and alternative pyrrolidones from biomass feedstock, with various sustainable routes proposed [73–76], such as starting from levulinic acid or its esters. A bio-based approach for 2-pyrrolidone involves a two-step enzymatic process that converts glutamic acid to γ-aminobutyric acid, followed by cyclization [62]. However, this method has limitations, including the need for precise pH control and expensive co-factors [62]. An alternative is the direct decarboxylation of glutamic acid using metal catalysts, which could offer a more feasible and economical solution and will be presented in the section related to the chemo-catalytic conversion [62].

Lactams and diamines such as cadaverine, 1,4-diaminobutane, ε-caprolactam and 2-pyrrolidone and its derivatives are as presented widely used N-chemicals that play a crucial role in various industrial applications with their large-scale production often based on fossil processes. In addition, amino alcohols and nitriles such as acetonitrile and acrylonitrile are also victims of such environmental impact, highlighting the urgent need for more sustainable processes to produce these N-chemicals. Therefore, there is a need to discuss their markets, production, etc., to see their economic potential.

### 3.3. Other N-chemicals

Other N-chemicals, such as nitriles and amino alcohols, show great potential for conversion from biomass to replace fossil derived ones [77,78]. Amino alcohols, which contain both amine and hydroxyl groups, [72] are used in pharmaceuticals, cosmetics, insecticides, and chiral auxiliaries [79–82]. Traditional synthesis methods involve either the direct hydrogenation of amino acids with metal hydrides or reactions between epoxides and amines, both relying on fossil-based compounds [65,80]. A more suitable method is the direct heterogeneous catalytic hydrogenation of amino acids into amino alcohols using biomass as feedstock, although catalyst deactivation due to the complex structure of amino acids poses a concern [79–83].

Nitriles, organic compounds with cyano functional groups, are prime candidates for biomass-based production, particularly for use in polymers (e.g., resins, fibers, and elastomers), pharmaceuticals, and agriculture [45]. Two key nitriles are acrylonitrile and acetonitrile [45]. To begin with, acrylonitrile is essential in acrylonitrile – butadiene – styrene (ABS) and styrene – acrylonitrile (SAN) production, with an annual production of 6.1 million tons in 2020 and a market size of 11,190 million USD in 2022 [45,84–86]. Current production involves the ammoxidation of propane and propylene using ammonia, highlighting the need for more sustainable, bio-based alternatives such as the ammoxidation of bio-derived alcohols and aldehydes like glycerol and allyl alcohols or direct conversions from nitrogen-containing compounds (e.g., amino acids) [45].

Furthermore, acetonitrile is another nitrile widely used in agriculture and pharmaceuticals but is primarily produced as a petrochemical by-product [45]. There is a need to develop sustainable production routes using ethanol, acetic acid, or similar compounds derived from lignocellulosic biomass or microalgae [45]. However, a more beneficial approach would involve using biomass components such as amino acids that already contain nitrogen, therefore reducing the need for additional nitrogen sources.

Consequently, as presented in this section, all the N-chemicals, in particular the diamines, lactams, amino alcohols, and nitriles mentioned above, would benefit from the sustainable production via the conversion of amino acids derived from nitrogen-rich biomass offered by chemo-catalytic heterogeneous catalysis. Therefore, the following section focuses on recent advances in catalytic systems that facilitate such a conversion.

## 4. Catalytic conversion of amino acids towards added value N-chemicals

While studies on the conversion of amino acids into the above-mentioned high-value products have primarily focused on enzymatic methods, the focus of our research is on chemo-catalytic conversion using different amino acids, proteins or hydrolysed proteins with homogeneous and heterogeneous catalysts. This decision is due to the challenges associated with enzymatic methods, such as enzyme efficiency and stability, high cost of required additives and wastewater treatment [46,62]. In addition, our investigation has found a significant gap in current research on chemo-catalytic conversion, which is the aim of this review.

The following section are categorized according to the catalysts into three groups: homogeneous catalysts, noble metals (e.g., ruthenium (Ru), rhodium (Rh), palladium (Pd), iridium (Ir), and platinum (Pt)) [87,88]), and non-noble metals (e.g., nickel (Ni), aluminum (Al), copper (Cu), or zinc (Zn) [89]). Both noble and non-noble metals are often supported on solid materials such as alumina ($Al_2O_3$), activated carbon (C), or other supports [90]. Primarily emphasize on heterogeneous

catalysts is due to a number of the advantages that poses, such as their easier separation and reusability compared to homogeneous catalysts, despite slightly lower conversions, the need for harsher reaction conditions, and the potential for active phase leaching [90]. A summary and discuss on homogeneous catalysis for the conversion of amino acids into N-chemicals follows.

### 4.1. Homogeneous catalysts

To understand the conversion of amino acid to high-value N-chemicals, studies have examined homogeneous catalysts such as bio-organocatalysts, reductive or oxidizing agents, and thermal decarboxylation where the initial research was conducted on the reductive agents.

Reductive agents have been extensively investigated in studies [79,91] reporting on amino alcohols derived from various amino acids or their ethyl esters. The yields of these amino alcohols varied directly with the reductive agents used, ranging from 50 % to 95 % [79,91]. Recent studies have highlighted the effectiveness of using reductive agent but also oxidizing agents and organocatalysts in the chemo-catalytic conversion of amino acids to N-chemicals was also examined.

Additionally, the study by Xie *et al.* [79] summarized oxidizing agents (e.g., peroxides) and organocatalysts like Schiff's bases, achieving the decarboxylation of amino acids into their corresponding amines with high yields of up to 99 % [79]. Further, the study by Dawes *et al.* [92] categorized oxidizing agents and organocatalysts as bio-organocatalysts, demonstrating the decarboxylation of amino acids such as glutamic acid, methylglutaminate, and L-phenylalanine into compounds like 3-cyanopropanoic acid or 3-cyanopropanoic methyl ester. These intermediates can be further converted into acrylonitrile phenethylamine with yields ranging between 70 % and 90 % [92]. The same review discussed thermal decarboxylation, such as high-temperature water treatment of phenylalanine to phenethylamine, achieving a 68 % yield with near-complete conversion [92]. This relatively low yield may be due to side reactions that form side products at elevated temperatures [92].

Similarly, studies also focused on converting L-lysine or its salts to ε-caprolactam using heterogeneous catalysts [55,61]. A patent by Frost [61] describes a two-step process using different catalysts at each step (see Table 1, entry 1). The first step involves cyclization or lactamization to form α-amino-ε-caprolactam achieving an excellent yield of 96 % (see Fig. 3C), followed by deamination (see Fig. 3C) to ε-caprolactam, reaching only a 75 % yield [61]. Similarly, a review by Liu *et al.* [55] reported medium to high yield (58 mol% to 87 %) for similar reactions, summarized in Table 1, entries 2 to 4, [55]. These varying yields could be attributed to the multifunctional nature of amino acid (e.g., L-lysine), as noted by Ma *et al.* [93].

As demonstrated above, early research primarily focused on the use of homogeneous catalysts, which achieved excellent yields (up to 99 %) of final N-chemicals but often lacked a detailed description of the catalytic mechanisms involved. Due to significant advantages and to address the current research of heterogeneous catalysis, we will further delve into details of heterogeneous catalysis in the following sections.

### 4.2. Noble metal catalysts

The chemo-catalytic conversion of amino acids into amino alcohols, diamines, and nitriles has predominantly focused on noble metal catalysts, with ruthenium (Ru) being the most commonly employed catalyst across various supports, which will be first discussed in more details. Numerous studies have also explored the potential of other noble metals for these transformations, highlighting the versatility and effectiveness of different catalytic systems.

#### 4.2.1. Ruthenium-based catalysts

Ruthenium catalysts have been widely used, either as homogeneous complexes or supported on solid substrates, to hydrogenate double bonds and oxygen-containing groups, facilitating the production of high-value chemicals [94]. For instance, Ru supported on carbon is versatile and finds applications across a wide range of reactions, but specifically, it is used for the hydrogenation of carbonyl compounds, including aldehydes and ketones, to their corresponding alcohols [95]. However, it can also be used in biomass conversions where it is particularly effective for the hydro(deoxy)genation (HDO) of carboxylic acids (e.g., lactic acid), where high temperatures (over 100 °C) are necessary to achieve high yield up to 90 % [19,82]. However, challenges such as the agglomeration of the Ru-(nano) particles during catalytic processes can reduce their efficiency and activity [93]. This section, therefore, focuses on the application of ruthenium (Ru) catalysts in converting various amino acids into the above-mentioned N-chemicals.

The conversion of amino acids using Ru catalysts has been extensively studied, with the common choice being 5 wt% Ru supported on carbon (Ru/C) [78,81,82,93,94,96–99]. This catalyst has been applied to various amino acids, including L-alanine and phenylalanine as shown in Table 2 [78,81,82,93,94,96–99]. Through hydrogenation, L-alanine and phenylalanine are converted into their corresponding amino alcohols (see Fig. 4), L-alaninol and 3-phenyl-2-(1H-pyrrol-1-yl) propan-1-ol, respectively (Table 2, entries from 1 to 6) [81–83,94,96,100]. Other amino acids, such as L-lysine, (pyro)glutamic acids, serine, and valine are similarly hydrogenated to produce amino alcohols (see Fig. 4) like L-lysinol (Table 2, entry 8) [78], 2-amino-1,5-pentanediol (Table 2, entry 12) [98], serinol (Table 2, entries 6 and 12) [81,98] and valinol (Table 2, entry 6) [81], respectively. Furthermore, a comprehensive overview of those conversion conducted on Ru-catalysed reactions will be summarized and discussed.

A study conducted on phenylalanine (Table 2, entry 1) [100] employed Ru-complexes with different ligands and protected amine group ($NH_2$) with a pyrrolyl group. This setup demonstrated that using a homogeneous Ru catalyst (ligand tris(*para*-fluorophenyl)phosphine (cod)(η3-methallyl)$_2$) and toluene as a solvent achieved a 58 % yield of 3-phenyl-2-(1H-pyrrol-1-yl) propan-1-ol, with high enantiomeric purity (89:11), under mild reaction conditions (120 °C and 40 bars of hydrogen as a reductive gaseous phase) [100]. The study emphasized that homogeneous catalysts present notable advantages over heterogeneous

**Table 1**
L-lysine (monohydrochloride) conversion to ε-caprolactam using homogeneous catalysts [55,61].

| Table entry | Intermediate | Homogeneous catalyst(s) | Solvent(s) | Reaction temperature (°C) | Yield (% or mol %) |
|---|---|---|---|---|---|
| 1 | α-amino-ε-caprolactam | Deamination: KOH and hydroxylamine-O-sulfuric acid | 1,2-propanediol | Lactamization: 190<br>Deamination: −5 | 75 |
| 2 | α-amino-ε-caprolactam | Lactamization: NaOH and $Al_2O_3$<br>Deamination: hydroxylamine-O-sulfuric acid | 1-butanol | Lactamization: 117<br>Deamination: room temperature | 87 |
| 3 | α-amino-ε-caprolactam | Lactamization and deamination: NaOH | ethylene glycol and water | Lactamization and deamination: 190 | 87 |
| 4 | – | Lactamization and deamination: cesium carbonate and propanoic acid | Acetonitrile | – | 58 mol% |

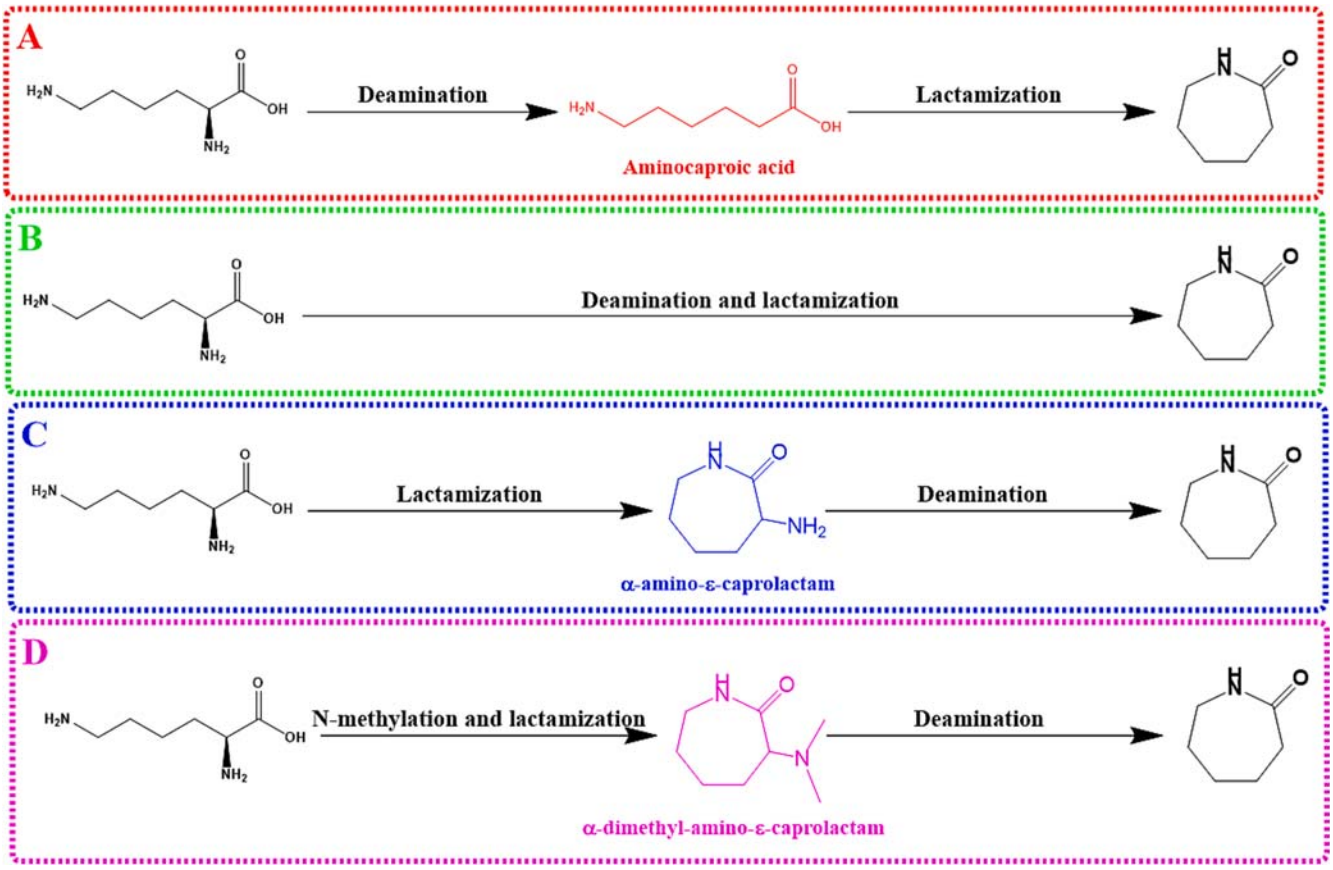


**Fig. 3.** Different routes from L-lysine to ε-caprolactam reported by [59,60].

catalysts, particularly their resistance to poisoning by sulfur-containing amino acids, which enhances their versatility for a wider variety of amino acids [100].

A handful of other amino acids were examined for hydrogenation in their corresponding amino alcohols, which have previously been recognized as potential N-chemicals for direct production from these amino acids. Those amino acids include L-alanine, L-lysine, (pyro)glutamic acids, serine, and valine (see Fig. 4) [78,81–83,94,96,98]. To clarify, the corresponding amino alcohols are L-alaninol (Table 2, entries from 2 to 6) [81–83,94,96] L-lysinol (Table 2, entry 8) [78], 2-amino-1,5-pentanediol (Table 2, entry 12) [98] serinol (Table 2, entries 6 and 12) [81,98] and valinol (Table 2, entry 6) [81]. Across these studies [78,81–83,94,96,98] a consistent finding was provided, where beneficial effect of adding mineral acids such as phosphoric ($H_3PO_4$) or sulfuric ($H_2SO_4$) acid to increase the yield or selectivity of amino alcohols was found. These acids lower the pH of the reaction mixture, which is crucial because the formation of amino alcohols raises the pH and slows the reaction due to unfavourable conditions for the typically zwitterionic nature of amino acids (see Fig. 5) [78,81–83,94,96,98]. Furthermore, the multifunctional character of amino acids with both carboxylic and amino groups necessitates acidic conditions to favour decarboxylation or hydrogenation into aldehydes or alcohols [78,81–83,94,96,98].

In general, most studies utilized water as the solvent, with reaction temperatures ranging from 50 °C to 180 °C, high hydrogen pressures of 17 to 134 bars, and reaction times from 0.75 to 64 h [78,81–83,94,96,98]. These conditions yielded good selectivity and conversion rates for amino alcohols ranging from 50 % to over 90 % [78,81–83,94,96,98]. One study [82] (Table 2, entry 4) highlighted the impact of reaction conditions on the hydrogenation of amino acids like L-alanine to L-alaninol. It was found that higher temperatures promote side reactions, such as racemization, resulting in the formation of D-alaninol instead of L-alaninol at 150 °C [78,82]. Similarly, the excessive hydrogen pressure (above 70 bars) was deemed detrimental as it could saturate the catalyst's active sites [82]. Moreover, the inclusion of secondary metals or metal oxides (e.g., Re or $Re_2O_7$) with Ru/C catalyst was shown to significantly reduce reaction times and temperatures enhancing overall efficiency [94] (Table 2, entry 5). The insights obtained from these studies provide valuable information for future research aimed at hydrogenation, particularly when amino acids are hydrogenated into diamines, which are also recognized as important N-chemicals due to their diverse applications and the current lack of sustainable production methods from nitrogen-containing compounds, particularly amino acids.

In this context, various reaction conditions were investigated for the HDO of the amino acids L-lysine (Table 2, entries 7 and 9) [93,99] and L-valine (Table 2, entry 10) [97] to produce the corresponding diamine, cadaverine (1,5-diaminopentane) (see Fig. 6C) and the amine, isobutylamine (see Fig. 6D), respectively. In HDO of the L-lysine or L-valine to cadaverine or isobutylamine water was used as a solvent, with reaction temperatures ranging from 150 °C to 260 °C under hydrogen pressures of 20–40 bars, and reaction times of 1 h to 15 h [93,97,99]. Both studies investigating cadaverine reported that selectivity was not higher than 51 % [99] or 54 % [93]. Initially, Ma *et al.* (Table 2, entry 9) reported a poor selectivity of cadaverine but to improve selectivity to up to 54 %, a second metal, Mn, was added to $RuO_2$/Beta [93].

Similarly, the second study also targeted cadaverine using a monometallic Ru catalyst. Under optimized conditions (water as a solvent, approximately 30 bars of hydrogen, reaction temperature of 200 °C and reaction time of 2 h) it achieved a high overall diamine yield of 94 %, but the selectivity to diamine like cadaverine was still only 51 %. Comparing these studies [93,99] suggests that using a bimetallic catalyst on zeolites (e.g., Beta) with Ru oxides ($RuO_2$) or mineral acid might be favourable for cadaverine production. Additionally, 1,5-diamnohexane was also targeted diamine [99] but it only was found in traces, with a yield of just

**Table 2**
Ru-based catalysts for amino acids conversion.

| Table entry | Reactant(s) | Ru loading (wt.%) | Other metal(s)/ support (s)/ligand(s) | Product(s) | Yield/ Selectivity/ conversion % or mol%) | Type of reaction | Notes | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | Phenylalanine (N-protected) | / | tris(*para*-fluorophenyl) phosphine (cod)($\eta_3$-methallyl)$_2$ | 3-phenyl-2-(1H-pyrrol-1-yl) propan-1-ol | 58 % | Hydrogenation | – | [100] |
| 2 | L-alanine | 5 | Carbon | L-alaninol | >90 % | Hydrogenation | acidic pH with $H_3PO_4$ | [96] |
| 3 | L-alanine | 5 | Carbon | L-alaninol | >90 % | Hydrogenation | acidic pH with $H_2SO_4$ | [83] |
| 4 | L-alanine | 5 | Carbon | L-alaninol | >70 % | Hydrogenation | acidic pH with $H_3PO_4$ | [82] |
| 5 | L-alanine | – | Re and $Re_2O_7$ Carbon | L-alaninol | High yield | Hydrogenation | – | [94] |
| 6 | Serine, Alanine and Valine | 5 | Carbon | Serinol, Alaninol and Valinol | >90 % | Hydrogenation | Selectivity for alanine and valine, acidic pH with $H_3PO_4$ | [81] |
| 7 | L-lysine | 5 | Carbon | Diamines (Cadaverine, 1,5-diaminohexane) | 51 % | Hydrodeoxygenation | Selectivity for diamine acidic pH with $H_3PO_4$ | [99] |
| 8 | L-lysine | 5 | Carbon | L-lysinol | 50 %-70 % | Hydrogenation | Yield at the scale-up, acidic pH with $H_3PO_4$ and $H_2SO_4$ | [78] |
| 9 | L-lysine | 5 | Mn Beta | Cadaverine | 54 % | Hydrodeoxygenation | Selectivity for cadaverine | [93] |
| 10 | L-valine | 5 | Carbon | Isobutylamine | 87 % | Hydrodeoxygenation | acidic pH with $H_3PO_4$ | [97] |
| 11 | Leucine | 5 | $\gamma$-$Al_2O_3$hydroxyapatite (HA) | Isovaleronitrile | 80 % | Oxidative decarboxylation | Selectivity, Ru $(OH)_x$ used | [101] |
| 12 | Serine (SE) and Glutamic acid (GA) | 5 | Carbon | Serinol and 2-amino-1,5-pentanediol | SE: 60 % GA: 40 % | Hydrogenation | Conversion | [98] |
| 13 | Glutamic Acid Pyroglutamic Acid | 5 | $Al_2O_3$ | 2-Pyrrolidone | 60 % | Hydrodeoxygenation Lactamization | – | [102] |

10 %.

Further study by Verduyckt *et al.* [97] found that lower hydrogen pressure and temperatures favourably influenced the HDO of amino acids (e.g., L-valine) to amines (e.g., isobutylamine) However, this process requires longer reaction times to achieve adequate yields of isobutylamine. Comparing the yields of (di)amines using monometallic Ru/C in studies focused on cadaverine [99] with those focused on isobutylamine [97] underscores the influence of the aliphatic side chain length on yield. Longer side chain with an additional amino group (e.g., L-lysine) showed lower yields of cadaverine (around 50 %) in [99] and 32 % found by Verduyckt *et al.* [97] in comparison to, shorter aliphatic side chains (e.g., L-valine) achieving higher yields (87 %) [97] even at lower temperature (150 °C) compared to a maximum temperature of 260 °C [99]. This indicates that steric hindrance from the aliphatic side chain may impact the decarboxylation efficiency of amino acids (e.g., L-lysine) when investigated using heterogeneous catalysts.

A similar study was conducted when compared to previous works [93,97,99], but the mechanism and final product differed. In this study, (pyro)glutamic acid (Table 2, entry 13) [102] was converted into the lactam 2-pyrrolidone, which is seen as one of the most promising N-chemicals to be produced directly from the amino acids (see Fig. 6A). Various metal catalysts (Rh, Pt, Ru, and Pd) supported on alumina were tested. In this context, side products included pyrrolidine and 5-methyl-2-pyrrolidone; however, 2-pyrolidone was reported as the main product [102]. This reaction achieved a maximum yield of 60 % when using Ru on alumina, with water as the solvent, under 20 bars of hydrogen in the gaseous phase, at a temperature of 160 °C, and over a reaction time of 2 h [102]. Although the reaction mechanism is similar to those in other studies [93,97,99], the initial step involves cyclization/lactamization (see Fig. 6A), which readily occurs once aliphatic amines are dissolved and heated up to 120 °C [102].

In contrast, to other reported reactions, this study used oxidative decarboxylation of leucine to form nitrile isovaleronitrile (Table 2, entry 11) [101]. Unlike the previous studies, this study also used water as a solvent but employed oxygen (around 30 bars) instead of hydrogen and used Ru oxides as catalysts under weak alkaline conditions, at temperatures ranging from 80 °C –150 °C, with reaction times of 24 h [101]. These reaction conditions present a significant advantage; the alkaline solution combined with Ru oxides facilitates the formation of isovaleronitrile by presenting amino acids in their anionic form (see Fig. 5), leading to the production of a carboxylate that more easily attaches to the Ru oxide active sides [101]. Additionally, oxygen in the gaseous phase is needed to form water as a side product in this transformation [101].

Research on noble metal catalysts has proven highly effective in converting amino acids into the N-chemicals as discussed, showcasing their ability to achieve high yields and selectivity. While ruthenium (Ru) has been the most commonly utilized catalyst due to its remarkable performance across various supports, other noble metals have also been explored for their catalytic potential in amino acids transformations to above-discussed N-chemicals.

#### 4.2.2. *Other noble catalysts*

Researchers have explored other noble metals for converting amino acids into high-value-added N-chemicals described earlier, focusing primarily on three amino acids: L-alanine, L-lysine, and (pyro)glutamic acid. The most efficient, selective, and active noble metal catalysts identified were Rh, Pt, Pd, and Ir on different supports (Table 3, entries 1–10) [19,55,59,60,62,80,103–105]. Firstly, we want to present the common use cases of the catalyst utilized in the conversions presented

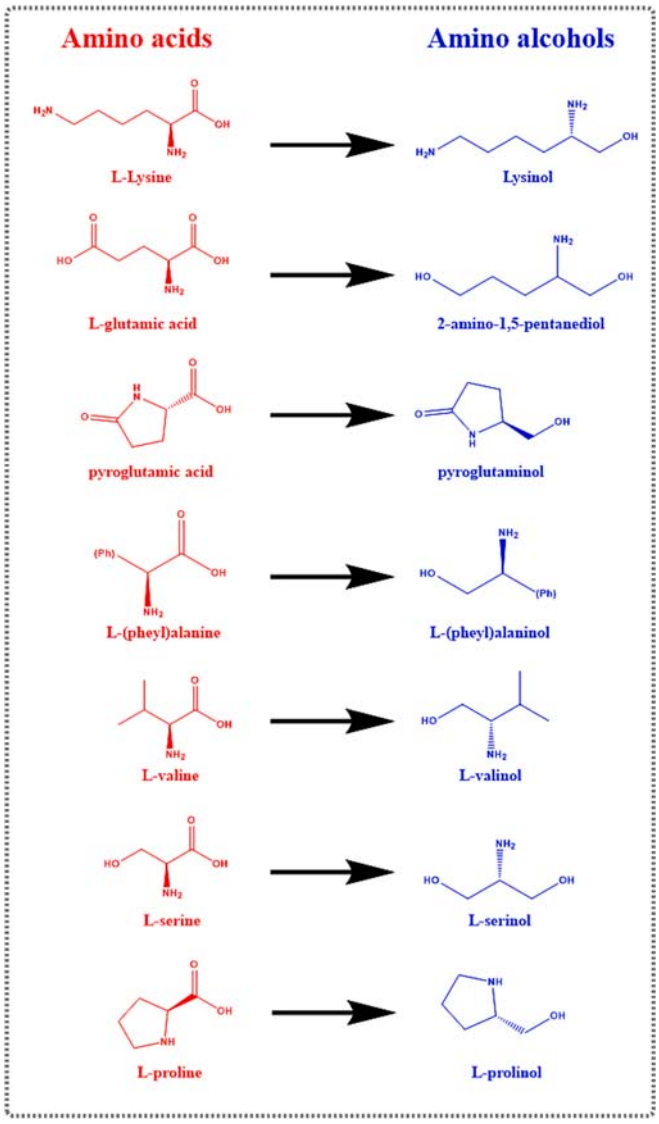


**Fig. 4.** Hydrogenation of different amino acids to their corresponding amino alcohols.

below. In this regard, Pt/C is frequently used in industry for heterogeneous catalytic reactions, in particular for the hydrogenation of carboxylic acids to alcohols and further conversion to alkanes with Pd/$Al_2O_3$ having a similar use case in the selective hydrogenation of carbonyl groups [95]. Moreover, this catalyst is also suitable for the dehydrogenation of alkanes and is used in hydrodenitrogenation, where it helps to remove nitrogen compounds from e.g., fuels and other products [95,106]. In addition, a combination of Rh and silica ($SiO_2$) is used for oxidation reactions, methanol synthesis, and hydroformylation [95]. These catalysts show use in numerous chemical transformations but can also be used for biomass-derived components such as amino acids in reactions similar to those mentioned above and will be discussed in the following section. A rhodium (Rh) based catalyst (Table 3, entries 1 and 2) combined with molybdenum oxide ($MoO_x$) on silica ($SiO_2$) was used for the hydrogenation of L-alanine towards amino alcohol (see Fig. 4), specifically L-alaninol [19,80]. Similar catalytic systems were also employed for the conversion of L-lysine to L-lysinol (Table 3, entry 3) [55,104], the transformation of (pyro)glutamic acid into amino alcohols, including 2-amino-1,5-pentanediol, pyroglutaminol, 2-amino-1-pentanol and 4-amino-1-pentanol or into lactam (prolinol) (Table 3, entry 6, see Fig. 4) [104] and the transformation of L-proline to L-prolinol (Table 3, entry 10, see Fig. 4) [107].

Furthermore, the consistent use of the Rh–$MoO_x$/$SiO_2$ catalyst across various studies highlights its adaptability in different reaction conditions involving the use of water as a solvent, reaction temperatures ranging from 30 °C to 140 °C, hydrogen pressure between 70 and 80 bar, and reaction times of up to 48 h for the hydrogenation of above-mentioned amino acids [19,55,80,104]. Nevertheless, also Pt in combination with $MoO_x$ on different support such as $Al_2O_3$ was utilized using water as a solvent, hydrogen pressure of 1 bar to 20 bars, reaction temperature of 70 °C to 120 °C and reaction times up to 5 h [107]. The results from these studies [19,80] align with those obtained using monometallic Ru/C catalysts [78,81–83,94,96,98], indicating that the bimetallic Rh–$MoO_x$/$SiO_2$ [19,80,104] or Pt–$MoO_x$/$Al_2O_3$ [107] catalysts does not provide a significant advantage in terms of yield for amino alcohols, such as L-alaninol, compared to the monometallic Ru/C catalyst. Instead, it demonstrates the versatility of heterogeneous catalysts for obtaining the same products (e.g., L-alaninol) through hydrogenation. Notably, comparable selectivity (around 95 %) for L-lysinol was observed in studies on L-lysine hydrogenation [55,104], consistent with other reports [19,80,104]. Additionally, in some cases, such as L-proline to L-prolinol utilizing Pt–$MoO_x$/ $Al_2O_3$, shows even poorer performance as indicated in Table 3, entry 10, showing only 48 %-59 % yield, which could be attributed to the fact that authors obtained the conversion of only around 70 % [107].

In light of these findings, consistent with previous findings [93,94,99], it was noted that the presence of a second metal (e.g., $MoO_x$ or Mn [93,99]) can enhance both the yield and selectivity, with yields/selectivities reaching up to 90 % for products such as L-alaninol, L-lysinol, 2-amino-1,5-pentanediol, pyroglutaminol, 2-amino-1-pentanol, and 4-amino-1-pentanol but low for L-prolinol which was 48 %-59 % [19,55,80,104]. Further investigation into (pyro)glutamic acid to 2-amino-1,5-pentanediol, pyroglutaminol, 2-amino-1-pentanol, and 4-amino-1-pentanol presented a potential solution to catalyst poisoning by sulphur-containing amino acids [104]. This was achieved by oxidizing thiol and thioether functional group via in situ formation of performic acid [104]. Additionally, this study also found the limitations of hydrogen pressure in hydrogenation of amino acids (e.g., (pyro)glutamic acid) to amino alcohols (e.g., 2-amino-1,5-pentanediol, pyroglutaminol, 2-amino-1-pentanol or 4-amino-1-pentanol) observed by Metkar *et al.* [78] and Jere *et al.* [82] due to poor hydrogen solubility in water, which was used as a solvent for the all the described conversions [104].

In addition to these advancements, recent studies have also explored the conversion of L-lysine into ε-caprolactam (Table 3, entries 4 and 5) via lactamization and deamination utilizing monometallic heterogeneous catalysts [59,60]. Both studies [59,60] focused on transforming L-lysine into ε-caprolactam via intermediate compounds such as

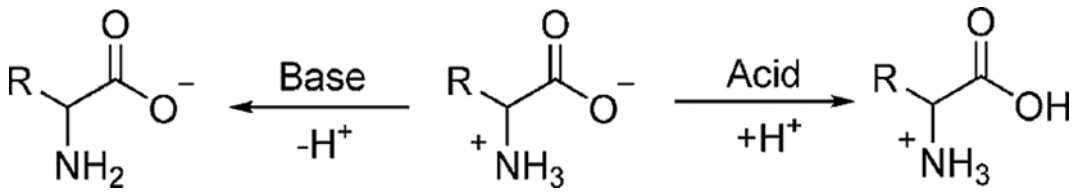


**Fig. 5.** Zwitterions of amino acids. Reproduced with permission from Tamura et al.[19], *Chem. Eur. J.*; published by WILEY-VCH Verlag GmbH & Co. KGaA, 2015.

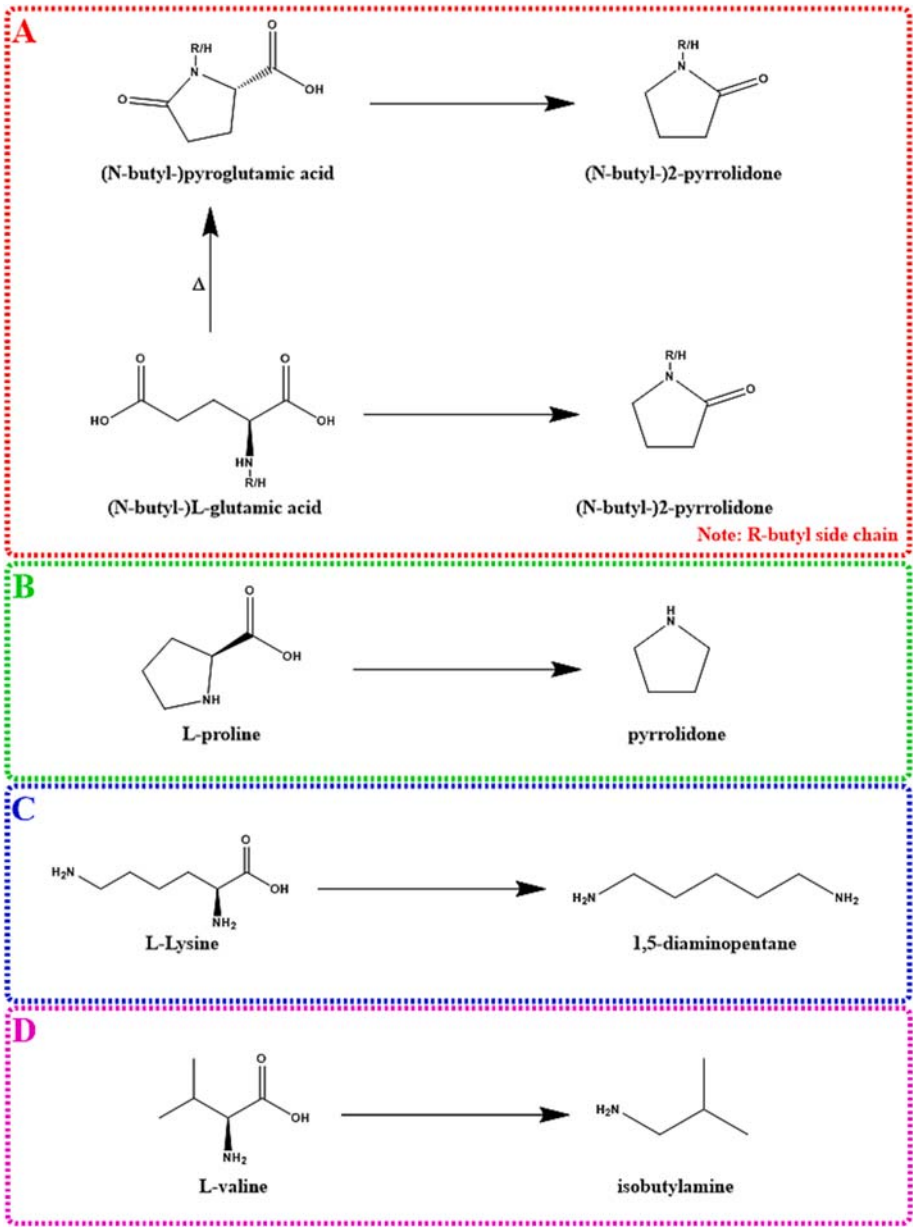


**Fig. 6.** Selective decarboxylation of A) (pyro)glutamic acid to 2-pyrrolidone, adopted with permission of Xie et al. [81], *J. Clean. Prod.*; published by Elsevier, 2023; B) L-proline to pyrrolidone, reprinted (adapted) with permission from [103]. Copyright © 2016 American Chemical Society; C) L-lysine to cadaverine, reprinted (adapted) with permission from [99]. Copyright © 2020 American Chemical Society, and D) L-valine to isobutylamine [97].

α-dimethyl amino ε-caprolactam, α-amino ε-caprolactam or amino-caproic acid (see Fig. 3A, B, C and D). The investigation by Sebastian *et al.* [59] used methanol as a solvent, operating at reaction temperatures between 235–250 °C, with a hydrogen pressure of 30 bars, and reaction times ranging from 6 to 8 h while the patent by Frost [60] used tetrahydrofuran, ethanol, or water as a solvent, with temperatures varying from 50 °C to 300 °C. Additionally, this study [60] also used a gas mixture of hydrogen and hydrogen sulphide, with hydrogen sulphide comprising up to 50 vol% of the gaseous phase and pressure reaching up to 207 bars, over an 8-h reaction time.

While both studies [59,60] reported moderate yields of ε-caprolactam, reaching 58 mol% with iridium (Ir) on zeolite H-beta-124 [59] and up to 65 % with Pt-S on activated carbon [60], they also presented significant opportunities for further optimization through advanced heterogeneous catalysts, such as bimetallic systems to enhance the yield of ε-caprolactam. However, the process conditions described in the patent [60] are not considered as environmentally friendly due to the high use of $H_2S$ in the gas phase, mainly to achieve catalyst sulfidation. Furthermore, the study by Frost [60] reported on the formation of another product, pipecolinic acid, in significant amounts (up to 65 %), when using a palladium on carbon as a catalyst.

Following these findings, Sebastian *et al.* [59] proposed three mechanistic pathways for the conversion of L-lysine to ε-caprolactam, as illustrated in Fig. 3; A) deamination of L-lysine followed by lactamization to ε-caprolactam, B) direct conversion to ε-caprolactam, C) lactamization followed by deamination, D) N-methylation and lactamization followed by deamination. Additionally, Sebastian *et al.* [59] provided potential strategies to improve the ε-caprolactam yield, which was reported at 58 mol%. The key parameters were identified that could significantly enhance the yield of ε-caprolactam which are related to optimizing the metal hydrogenation active sites, incorporating strong Brønsted acidic sites, utilizing catalyst with larger pore size, adjusting the Si/Al ratio, optimizing the iridium loading, and fine-tuning hydrogen pressure (around 30 bars) [59].

**Table 3**
Other-noble metal catalysts for the conversion of amino acids.

| Table entry | Reactant(s) | Loading/ metal | Other metal(s)/ support(s) | Product(s) | Yield/ selectivity/ conversion (% or mol%) | Type of reaction | Notes | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | L-alanine | 4 wt% Rh | $MoO_x$ $SiO_2$ | L-alaninol | >90 % | Hydrogenation | acidic pH with $H_3PO_4$ | [80] |
| 2 | L-alanine | 4 wt% Rh | $MoO_x$ $SiO_2$ | L-alaninol | >80 % | Hydrogenation | Selectivity, acidic pH with $H_3PO_4$ or $H_2SO_4$ (preferred) | [19] |
| 3 | L-lysine | Rh | $MoO_x$ $SiO_2$ | L-lysinol | 87 % | Hydrogenation | Selectivity, acidic pH with $H_3PO_4$ | [55,104] |
| 4 | L-lysine | 2 % Ir | H-beta-124 | ε-caprolactam, α-dimethyl amino caprolactam | 58 mol% | Deamination Lactamization | – | [59] |
| 5 | L-lysine or its salts α-amino-caprolactam | 8 mol% Pt Pd | Carbon | ε-caprolactam pipecolinic acid | 15 %-65 % 65 % | Deamination Lactamization | Presulfided catalyst, mixture of $H_2S$ and $H_2$ as gaseous phase | [60] |
| 6 | Glutamic acid Pyroglutamic acid | 4 wt% Rh | $MoO_x$ $SiO_2$ | 2-amino-1,5-pentanediol, 2-amino-1-pentanol, 4-amino-1-pentanol, pyroglutaminol, prolinol | 99 % | Hydrogenation | Selectivity, acidic pH with $H_3PO_4$ | [104] |
| 7 | Glutamic acid Pyroglutamic acid | 5 wt% Pd | $Al_2O_3$ | 2-pyrrolidone | 70 % | Decarboxylation | acidic pH with $H_3PO_4$ | [62] |
| 8 | Glutamic acid | 5 wt% Pd | $Al_2O_3$ | N-butyl-2-pyrrolidone | 82 % | N-alkylation Decarboxylation | Alkaline pH with ammonia | [105] |
| 9 | L-proline | 5 wt% Pd | 3.27 wt% Pb $ZrO_2$ | pyrrolidone | 95 % | Hydrodeoxygenation | Selectivity, use of the catalyst with better dispersion of Pb, acidic pH with $H_3PO_4$ | [103] |
| 10 | L-proline | 5 wt% Pt | $MoO_x$ $Al_2O_3$ | L-prolinol | 48 %-59 % | Hydrogenation | acidic pH with $H_3PO_4$ | [107] |

Similar studies also targeted other lactams described earlier (Table 3, entries 7 and 8) [62,105] where (pyro)glutamic acid was investigated for the conversion to (N-butyl-)2-pyrrolidones (see Fig. 6A) using palladium (Pd) catalyst supported on alumina ($Al_2O_3$). The first study focused on using amino acid in its native form [62], while the second study [105] involved N-alkylation to protect the amino group. In both cases, the reaction conditions included water as the solvent, reaction temperatures of 175–275 °C, nitrogen as the gaseous phase at pressures of 6–40 bars, and reaction times of around 6 h [62,105]. These studies [62,105] yielded results similar to previous findings [78,81–83,94,96,98], reporting on the side products such as propionic acid and ethane resulting from the degradation of 2-pyrolidone or (pyro) glutamic acid.

The selection of acidic supports played a crucial role in the reaction efficiency, as alumina ($Al_2O_3$) outperformed silica ($SiO_2$), yielding higher product amounts, which suggests that decarboxylation proceeds more efficiently on acidic supports [62]. Additionally, when N-alkylation was performed using different aldehydes or ketones, the steric hindrance effect of the amino acid side chain was observed [105]. However, factors such as pH of the solution, reaction time, temperature, and the concentration of the aldehydes/ketones significantly influence N-alkylation of the amino acids [105]. Notably, N-butyl-2-pyrrolidone showed higher yields compared to products without the additional alkyl group [105]. Additionally, it was observed that increasing the pH to more alkaline conditions led to higher yields of N-butly-2-pyrolidone [105], contrasting with previous report [62]. This enhancement might be due to (pyro)glutamic acid existing in a carboxylate form at alkaline pH (see Fig. 5), facilitating lactamization and decarboxylation in combination with the $Pd/Al_2O_3$ catalyst [62,105].

Overall, palladium on alumina ($Pd/Al_2O_3$) demonstrated superior performance for the conversion of (pyro)glutamic acid to 2-pyrrolidone, achieving yields of 70 % [62] and 85 % [105], compared to ruthenium on alumina ($Ru/Al_2O_3$) [102], which yielded only 60 %. Further comparison with another study [103] implementing water as a solvent, with up to 15 bars of hydrogen in the gaseous phase, temperatures ranging from 225 °C to 245 °C, and reaction times of 1 to 24 h (Table 3, entry 9) [103] indicated that bimetallic catalysts, such as $Pd–Pb/ZrO_2$ and supports like zirconia ($ZrO_2$) provided even better selectivity (N-butyl-)2-pyrrolidone (81 % [62] and 90 % [105]) and pyrrolidone (95 % [103]). These findings suggest that bimetallic catalysts are more effective for the decarboxylation of L-proline or (pyro)glutamic acid to (N-butyl-)2-pyrrolidone and pyrrolidone.

Further investigation into the preparation methods of the bimetallic catalyst ($Pd–Pb/ZrO_2$) for the HDO of L-proline to pyrrolidone was influenced by the dispersion of Pd particles which led to enhanced selectivity (from 50 % to 67 %) towards pyrrolidone [103]. Additionally, catalytic pathways from L-proline to pyrrolidone via HDO showed that pyrrole was an intermediate product in the initial step when using monometallic catalysts [103]. In contrast, with bimetallic catalysts (e.g., $Pd–Pb/ZrO_2$), pyrrolidone was directly formed through $CO_2$ removal and subsequent hydrogenation of double bonds [103].

The noble metals investigated have demonstrated strong catalytic performance in various transformations of amino acids into the above-described N-chemicals. However, further exploration of these conversions could benefit from the use of non-noble metal catalysts, which offer advantages in terms of lower cost and greater availability [108]. Therefore, in the following section, we will delve deeper into the various non-noble metals studied, examining their catalytic performance and potential applications in this field.

### 4.3. Non-noble metal catalysts

Non-noble metal catalysts offer a cost-effective and readily available alternative to noble metal catalysts, demonstrating competitive catalytic

activity in certain applications [108]. In the industrial processes, catalysts made of non-noble metals are frequently used in heterogeneous catalysis, in particular, Ni and Co as bimetallic catalysts, with molybdenum (Mo) as the second metal on alumina ($Al_2O_3$) [95]. These presulphided catalysts are particularly suitable for hydrodesulphurisation and hydrodenitrogenation, in which nitrogen and sulphur elements are removed from fuels, increasing their quality [95,106]. In addition, Ni and Co can be used as monometallic catalysts on alumina for the selective hydrogenation for the reduction of carbonyl groups such as aldehydes, alcohols and alkenes [95]. Furthermore, their use can also be in the biomass conversion, where one example of such non-noble metal catalysts was used in a study on oxidative decarboxylation of L-phenylalanine to produce bio-based nitriles (see Table 4 entry 1) [109]. The reaction was carried out using a slightly alkaline Ni–Al-based catalyst supported on $WO_4$ and layered double hydroxide (LDH) [109]. Additionally, ammonium bromide ($NH_4Br$) was used as a weak acid instead of a stronger mineral acid, with the reactions conducted at room temperature and atmospheric pressure [109].

Under these reaction conditions, carboxylate deposits were observed on the catalyst's surface, which negatively affected the surface area and catalytic activity [109]. This issue was significantly reduced by the addition of hydrogen peroxide, which helped in maintaining catalyst efficiency [109]. Additionally, a key mechanistic insight (see Fig. 7) was found where LDH support facilitated two main reactions: oxidative decarboxylation and bromination [109]. However, the bromine introduced during the reaction was later eliminated, leading to the formation of an aldehyde intermediate.

Further improvement in catalyst efficiency not only facilitated these mechanistic pathways but also set the stage for the oxidative decarboxylation reaction using the non-noble bimetallic Ni–Al-based catalyst, which achieved impressive results with 99 % selectivity towards nitriles, such as phenylacetonitrile [109]. This performance surpassed that of previously studied [101] monometallic noble metal catalysts, such as ruthenium oxide on carbon, which achieved only 80 % selectivity for nitriles like isovaleronitrile [109]. Moreover, these findings underscore the potential of non-noble bimetallic catalysts to offer comparable or even superior catalytic performance to noble metal catalysts in certain chemical transformations. In addition, the use of monosodium glutamic acid under similar reaction conditions resulted in the production of 3-cyanopropionate with a 99 % yield [109]. Such a product is a valuable N-chemical for use as a precursor for the production of acrylonitrile, succinonitrile, and adiponitrile, which are important building blocks in the production of various polymers and other high-value chemicals [109].

Further research has also been conducted on the conversion of amino acids to amino alcohols, which have already been extensively investigated using noble metal catalysts. Nevertheless, the exploration of non-noble metal catalysts was also investigated for the L-phenylalanine in its ester form (L-phenylalalinate), to be converted to L-phenylalaninol

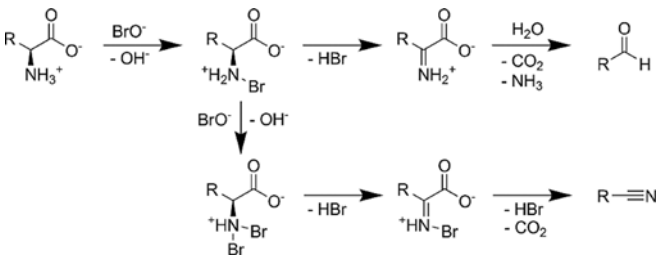


**Fig. 7.** Proposed mechanism of oxidative decarboxylation of L-phenylalanine to its corresponding aldehyde and nitrile. Reproduced with permission from Claes et al. [109], *ChemSusChem.*; published by WILEY-VCH Verlag GmbH & Co. KGaA, 2015.

using copper (Cu)-based catalysts, as described in two studies (Table 4, entries 2 and 3) [65,110]. These studies explored Cu catalysts with different supports, namely $Zr_{0.3}Mg_xAlO_y$ [110] and $ZnO/Al_2O_3$ [65], by varying the composition of the support. Optimal performance for the $Zr_{0.3}Mg_xAlO_y$ catalyst was achieved with a $Mg^{2+}/Al^{3+}$ ratio of 0.1, where higher magnesium content increased catalyst stability but reduced the number of active Cu sites [110].

At the same time second study [65] found $ZnO/Al_2O_3$ ratio of 0.3 to be optimal as ZnO significantly influenced the catalyst's physicochemical properties. Further testing the catalyst's performance under reaction conditions – using ethanol as a solvent, temperatures ranging from 70 to 150 °C with hydrogen pressure up to 60 bar and reaction times of 2 to 10 h – showed addition of the ZnO to the $Cu/Al_2O_3$ significantly improved chemoselectivity towards L-phenylalaninol with variation leading up to similar trends as previously reported by other studies [65,78,82,97,100].

On the other hand, increasingly enough, the catalyst amounts up to a ratio of 1.0:1.5 with L-phenylalalinate, positively impacted the yield of L-phenylanalinol, though excessive amounts promoted the formation of side products [65]. Further, authors also suggested that enhancing the surface area of the Cu catalyst could further improve yields, compared to the poorer performance by lower surface area reported in similar study (Table 4, entry 2) [65]. Final yields of L-phenylalaninol reached 91.1 % [110] and 69.2 % [65], respectively, outperforming noble monometallic Ru complexes, which only reached yield of 58 % of 3-phenyl-2-(1H-pyrrol-1-yl) propan-1-ol [100]. Additionally, pyroglutamic acid (Table 4, entry 4) [77] was investigated for conversion to its corresponding amino alcohol, pyroglutaminol, (see Fig. 4) using Ni-based catalysts on different supports such as $SiO_2$, $Al_2O_3$, $CeO_2$, $TiO_2$, $Nb_2O_5$, and $ZrO_2$. It was shown that the $Ni/SiO_2$ catalyst [77] possessed the highest performance using water as a solvent, at a temperature of 230 °C, under 31 bars of hydrogen, over an 8-hour reaction period, while at the same time displaying similar trends to those reported in other studies [78,82,100].

Furthermore, a similar reaction using a bimetallic catalyst on silica

**Table 4**
Non-noble metal catalysts for amino acids conversion.

| Table entry | Reactant(s) | Loading/ metal | Other metal (s)/ support(s) | Product(s) | Yield/ selectivity/ conversion (% or mol%) | Type of reaction | Notes | Reference |
|---|---|---|---|---|---|---|---|---|
| 1 | L-phenylalanine | Ni | Al LDH, $WO_4$ | Nitriles | 90 % | Oxidative decarboxylation | Tungstate loading was 12 % based on total AEC (anion exchange capacity), slightly acidic condition | [109] |
| 2 | L-phenylalanine | Cu | $Zr_{0.3}Mg_xAlO_y$ | L-phenylalaninol | 91.1 % | Hydrogenation | The best ratio between $Mg^{2+}/Al^{3+}$ was 0.1 | [110] |
| 3 | L-phenylalaninate->ester of L-phenylalanine | 34.4–49.9 wt% Cu | $ZnO/Al_2O_3$ | L-phenylalaninol | 69.2 % | Hydrogenation | The best ratio between the metals Cu/Zn/Al 1.0: 0.3: 1.0, | [65] |
| 4 | Pyroglutamic acid | 10 wt% Ni | $SiO_2$ | Pyroglutaminol | 73 % | Hydrogenation | – | [77] |

reported a higher yield of 99 % compared to the 73 % yield in the current study [77,104]. Furthermore, pyroglutamic acid, the cyclic form of glutamic acid was used instead of aliphatic [77] while employing a monometallic Ru/C catalyst for the production of 2-amino-1,5-pentanediol, yielding less than 40 % conversion [98]. Consequently, such findings underscore the necessity of either using mineral acid to achieve a more acidic environment, or a bimetallic catalyst is essential to facilitate the hydrogenation of amino acids to amino alcohols [77].

Research on the catalytic conversion of amino acids to amino alcohols, lactam and diamines has identified several paths to produce the valuable N-chemicals described above. In these studies, selection of catalyst and reaction conditions found to be crucial factor. To fully understand these catalytic systems the mechanisms and kinetics need to be further investigated. It is important to understand how amino acids interact with the catalyst surface and what influence they have on the reaction rate. This will provide us with further information for the optimisation of the catalytic systems to achieve higher yields and selectivity for the value-added N-chemicals.

## 5. Conversion of amino acids: Mechanism and kinetics

Multiscale modelling is applied across three distinct scale levels: atomic, meso, and macro scale, as illustrated in Fig. 8. In particular, the most relevant is meso scale is microkinetic modelling (MKM) which focuses on transport phenomena and is a fundamental tool for investigating various biomass conversion processes [111]. Kinetic data derived from MKM are crucial for understanding and determining reaction mechanism between reactants and catalysts [112].

Microkinetic modelling (MKM) is a powerful tool used for providing a detailed kinetic evaluation of chemical reaction by considering each individual reaction step rather than combining them into a single rate constant [113]. In the context of heterogeneous catalysis, MKM typically involves three fundamental steps: (I) adsorption of the reactants onto the catalyst surface, (II) surface reaction between adsorbed species, (III) desorption of the products from the catalyst surface [113]. Additionally, MKM accounts for transport phenomena that can influence the reaction kinetics [113]. To accurately model the kinetic behaviour of the reaction mechanism using MKM, several parameters are essential, including pre-exponential factors, adsorption and desorption coefficients, active side coverage on the catalyst, and activation energies [113]. To clarify, data related to adsorption and desorption process may be obtained experimentally or theoretically calculated [113]. Moreover, other parameters, such as reaction rates and activation energies, can be experimentally determined by conducting experiments under various reaction conditions (e.g., different temperature and reaction times) and by characterizing the catalyst and other components of the reaction system [113]. Before exploring the specific kinetic parameters associated with the conversion of amino acids to above- described N-chemicals, we will first briefly touch on theoretical overview of kinetic evaluation.

The simplest and most initial approach for the kinetic evaluation of reactions using MKM us the power-law kinetic model [112]. Assuming a second-order reaction, the power-law equation can be expressed as shown in Eq. (1) [112]:

$$-r = kC_A^n C_B^m \tag{1}$$

where $r$ represents the reaction rate, $C_A$ is the concentration of reactant A, $C_B$ is the concentration of reactant B, and $n$ and $m$ are the reaction orders with respect to reactants A and B, respectively [112]. This expression is applicable only to a limited set of reactions but can be extended in more complex kinetic evaluation to account for effects such as mass or heat transfer, as well as catalyst deactivation [112].

For a more comprehensive kinetic analysis, which includes scenarios like catalyst saturation, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model is often employed, and can be formulated as shown in Eq. (2) [112]:

$$r = \frac{(kineticterm) \bullet (thremodynamicdrivingterm)}{(adsorptionorsideblockingterm)^n} \tag{2}$$

where $r$ represents the reaction rate, the *kinetic term* is the forward rate constant of the rate-determining reaction, and the *thermodynamic driving term* indicates how close the overall reaction is to thermodynamic equilibrium [112]. The parameter $n$ is the number of surface-active sides involved in the rate-determining reaction [112]. Compared to the

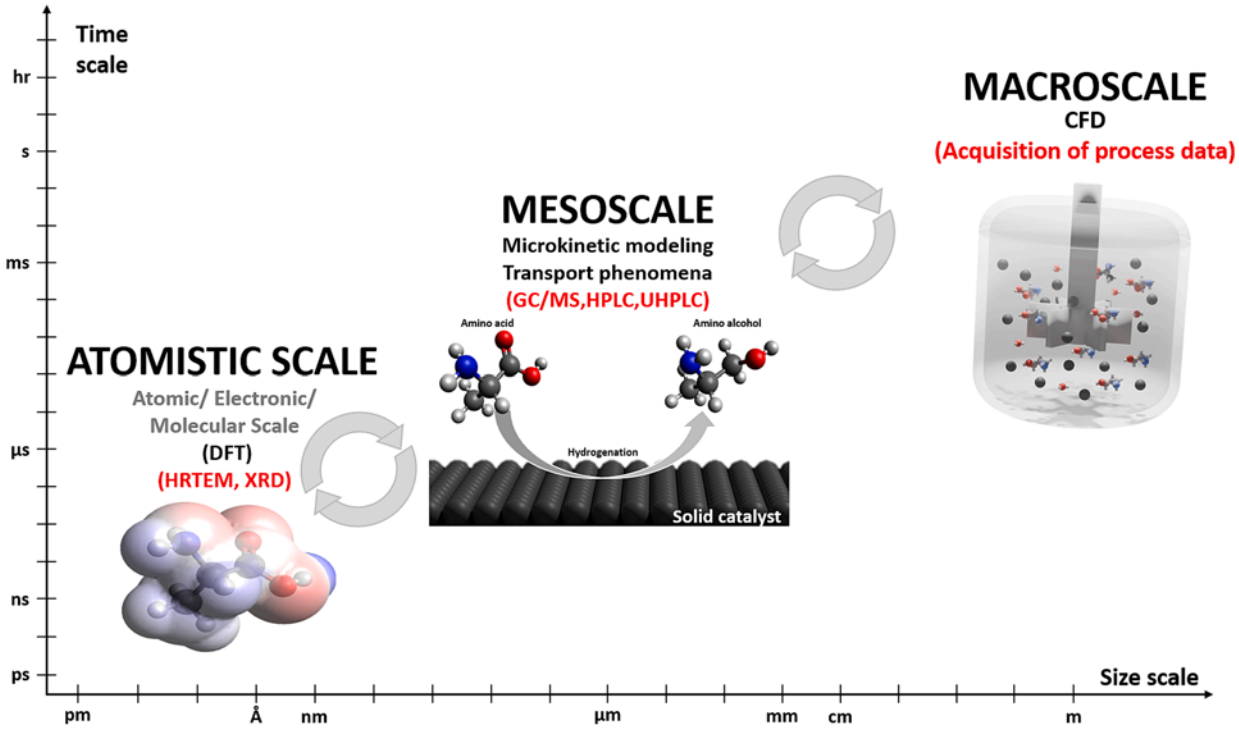


**Fig. 8.** Multiscale modelling approach for the conversion of amino acids to high-value N-chemicals.

power-law model, the LHHW expression is more versatile and can be adapted to a broader range of the reactions [112].

Further comprehensive understanding of the chemo-catalytic conversion kinetics of amino acids while employing the presented power-law or Langmuir-Hinshelwood–Hougen-Watson (LHHW) model is limited due to a lack of detail, particularly in the mechanistic steps that drive catalytic conversion. This large knowledge gap resulting from the lack of studies also leaves a significant uncertainty that makes it interesting to explore further. This gap is a bottleneck to new information for future studies, which could open up numerous new opportunities and advances in the field of chemical engineering for amino acid conversion to N-chemicals. To effectively bridge the different scales, an integrated multiscale modelling approach with a focus on microkinetic modelling is crucial as it provides a more comprehensive understanding of the chemo-catalytic conversion kinetics of amino acids. It not only addresses the current knowledge gaps in the mechanistic steps and kinetic of catalytic conversion but also reduces uncertainties, opening up the exploration of amino acid conversion research in chemical engineering. With a focus on the conversion of amino acids into high value-added N-chemicals emphasised in the section on their importance and value, the subsequent sections cover state-of-the-art reaction mechanisms, particularly the hydrogenation and decarboxylation of amino acids, and their (micro)kinetics, where simple models such as the Arrhenius plot and more advanced models such as power-law kinetics and the Langmuir-Hinshelwood–Hougen-Watson (LHHW) model have been most widely used.

### 5.1. Hydrogenation mechanism and kinetics

The hydrogenation mechanism of amino acids such as L-alanine, to amino alcohols, like L-alaninol (see Fig. 4) was examined in a study by Jere *et al.* [82], which proposed that the hydrogenation mechanism begins with the formation of 1,1-diol intermediate. This intermediate then undergoes dehydration to form an aldehyde, which is finally hydrogenated into the corresponding alcohol [82]. It was observed that the dehydration of 1,1-diol and the subsequent hydrogenation of the aldehyde proceed rapidly compared to the initial 1,1-diol formation step, a conclusion also supported by other studies [82,96]. Further mechanistic investigations [19,80,98] focused on the conversion of amino acids, including glutamic acids and L-alanine (see Fig. 4), to their corresponding amino alcohols, such as 2-amino-1,5-pentanediol and L-alaninol, respectively. These studies highlighted strong adsorption of amino acids onto the surface of both monometallic (Ru/C) [98] and bimetallic (Rh–$MoO_x$/$SiO_2$) [19,80] catalyst.

Further research into the hydrogenation of glutamic acid [98] revealed competition between hydrogen molecules and amino acids molecules for active sites on the Ru catalyst. However, this competitive adsorption could be mitigated by increasing the reaction temperature (e.g., 130 °C), which enhance the overall conversion rate towards amino alcohols like 2-amino-1,5-pentanediol (see Fig. 4) [98]. Similar study [81] observed comparable competition for Ru active sites, but in this case, it occurred between the different amino acids, such as L-alanine, serine, and valine, (Fig. 4), which were hydrogenated to produce L-alaninol, serinol, and valinol, respectively. Further investigation found significant conversion rate reduction for one amino acid while another is present, presenting a challenge when using hydrolyzed proteins—composed of mixed amino acids—as feedstocks for producing high-value N-chemicals [81]. This finding underscores the need to separate hydrolyzed proteins into individual amino acids before further conversion.

This competition for active sites not only presents the challenges in optimizing hydrogenation but also leads to insights about the distinct adsorption behaviours of amino acids and hydrogen on the catalyst surface. While exploring adsorption behaviours it was demonstrated that amino acids and hydrogen interact with different active sides on the catalyst [81]. Specifically, hydrogen adsorption and subsequent dissociation occur in the interstices of metal (Ru) atoms, while amino acids adsorption, including L-alanine, valine, and serine, takes places above the Ru active sites, with valine showing the highest affinity for adsorption on Ru/C catalyst [81]. Similar observation was reported in study [96], where $S_1$ active site was found to be associated with the adsorption of both amino acids and phosphoric acid ($H_3PO_4$) due to their acidic nature. As a result, this information plays a vital role in improving the kinetic modelling of the hydrogenation of amino acids into N-chemicals, such as amino alcohols.

Kinetic modelling using the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model has been employed to describe the hydrogenation of various amino acids, including glutamic acid, L-alaninol, valine, and serine (see Fig. 4), to their corresponding amino alcohols, such as 2-amino-1,5-pentanediol, L-alaninol, valinol and serinol, respectively [81,82,96,98]. These studies used monometallic Ru/C under similar reaction conditions [81,82,96,98]. Initial investigations into the hydrogenation of glutamic acid and serine into their respective amino alcohols reported reaction orders ranging from 0 to 1, consistent with the typical first-order kinetics observed for hydrogenation reactions [98].

But on the other hand, kinetic evaluations for the hydrogenation of other amino acids adopted different assumptions. One study [81] simplified the model by not accounting for all protonated forms of the amino acids and phosphoric acid, while another study [96] included these forms. Therefore, it is difficult to fully understand kinetic behind the hydrogenation of amino acids to amino alcohols but some correlation between the structures of different amino acids and their activation energies ($E_a$) can be made, where it is suggested that the side chain length and structure influence catalytic performance. For instance, valine, with an additional methyl group, exhibited a higher activation energy (95.5 kJ $mol^{-1}$ [81]) compared to L-alanine (88.5 kJ $mol^{-1}$ [81] and 81.5 kJ $mol^{-1}$ [96]), likely due to steric hindrance from the side chain. The reaction rate constant ($k$) for valine (0.0015 kmol $(kg_{cat}{\cdot}h)^{-1}$, at 130 °C) was also significantly lower than for L-alanine (0.016 kmol $(kg_{cat}{\cdot}h)^{-1}$, at 130 °C), further indicating slower catalytic conversion [81]. However, the presence of a functional group, such as hydroxyl group serine's aliphatic side chain, enhanced catalytic conversion, as evidenced by a higher rate constant (0.018 kmol $(kg_{cat}{\cdot}h)^{-1}$, at 130 °C), compared to L-alanine [81]. However, serine showed a slightly lower activation energy (83.1 kJ $mol^{-1}$) [96], suggesting that the hydroxyl group positively influences the activation energy by reducing it, facilitating easier catalytic conversion.

Similar kinetic evaluations for L-alanine hydrogenation to L-alaninol conducted by other studies [96] reported comparable reaction rate constant (0.012 kmol $(kg_{cat}{\cdot}h)^{-1}$ at 100 °C) and activation energy (81.5 kJ $mol^{-1}$) to those found by other researchers (0.016 kmol $(kg_{cat}{\cdot}h)^{-1}$ at 130 °C and 88.5 kJ $mol^{-1}$) [81]. The differences in $k$ and activation energy between these studies [81,96] were attributed to variations in reaction temperature, with higher temperatures favouring hydrogenation of amino acids to amino alcohols. Additionally, several effects on conversion rates were observed [96]. To begin with, higher concentrations of phosphoric acid, added to stabilize L-alanine in its protonated form, where expected to enhance hydrogenation. However, this addition actually decreased conversion rates due to active site saturation, a phenomenon observed previously [82], but was explained more comprehensively with insights into active site coverage (75 % at lower pressure versus 77 % at higher pressure) [96]. While increased temperature is known to improve conversion rates, the effect of hydrogen pressure on kinetics for amino acid conversion to value-added chemicals is less reported [96]. This study [96] found minimal effect of elevated hydrogen pressure, corroborated by active site coverage data, which showed little change with pressure variations. Poor hydrogen solubility in water, commonly used as a solvent, might also explain this hydrogen pressure limitation [104]. Notably, an 8 % yield was achieved without added phosphoric acid, likely due to the presence of acid sites on the activated carbon still facilitating amino acid conversion to amino alcohols [96].

Further investigation of hydrogenation of the amino acids is presented in the study investigating non-noble Cu-based catalysts on different supports $Zr_{0.3}Mg_xAlO_y$ ($Mg^{2+}/Al^{3+}$ ratio 0.1) [110] and ZnO/$Al_2O_3$ (ZnO /$Al_2O_3$ ratio 0.3) [65], where significant increases in reaction rates under identical conditions (110 °C, water, 40 bars of hydrogen, 5-hour reaction time) was demonstrated. A system utilizing $Zr_{0.3}Mg_xAlO_y$ ($Mg^{2+}/Al^{3+}$ ratio 0.1) achieved significant higher yields of around 91 % [110] compared to approximately 70 % for ZnO/$Al_2O_3$ [65]. These findings highlights that non-noble catalysts can achieve yields comparable to those of Ru-based catalysts (Table 2, entries 1–4) and other noble metal catalysts (Table 3, entries 1 and 10), though they require more complex support preparation.

Not only the effect of support on the hydrogenation of the amino acids to amino alcohols were investigated but also the influence of a second metal, $MoO_x$, on the catalyst Rh/$SiO_2$ in the hydrogenation of L-alanine to L-alaninol was investigated by [19,80]. Findings suggest that $MoO_x$ plays a crucial role in enhancing the catalytic performance by forming hydrogen bonds (see Fig. 9) between the $MoO_x$ sites and the carboxylic group of the amino acid, such as L-alanine [19,80]. This interaction facilitates the preferential adsorption of amino acids via their carboxylic group, leading to selective hydrogenation of the carboxylic group to a hydroxyl group while leaving the amino group intact (see Fig. 9) [19,80].

A more detailed mechanistic study of amino acids adsorption and conversion indicated that the rate-determining step in this hydrogenation process involves a hydride attack on the carbonyl group, which is formed during the heterolytic dissociation of hydrogen (see Fig. 9 steps II and III) [19,107]. Unlike traditional pathways where the carboxylic group is converted to an aldehyde via acyl (e.g., acetyl) intermediates, the catalyst Rh–$MoO_x/SiO_2$ bypasses the formation of acyl (e.g., acetyl) adspecies, directly hydrogenating the carboxylic group to aldehyde (see Fig. 9) [19]. This direct conversion provides a significant mechanistic advantage, ensuring selective hydrogenation without over-hydrogenation of amino acids L-alanine to L-alaninol [19].

The selective nature of this bimetallic catalyst is further enhanced by the adsorption behaviour of the hydroxy group of the resulting amino alcohol (e.g., L-alaninol) [19]. This adsorption occurs on $MoO_x$ sites, which shifts the amino alcohol away from Rh active sites, preventing further hydrogenation (see Fig. 9 steps V and VI) [19]. Such selective hydrogenation significantly improves the catalytic efficiency of Rh–$MoO_x/SiO_2$, demonstrating five times higher activity for the hydrogenation of α-amino acids compared to monometallic catalysts. This increased activity is attributed to the synergistic interaction between Rh and $MoO_x$ [19].

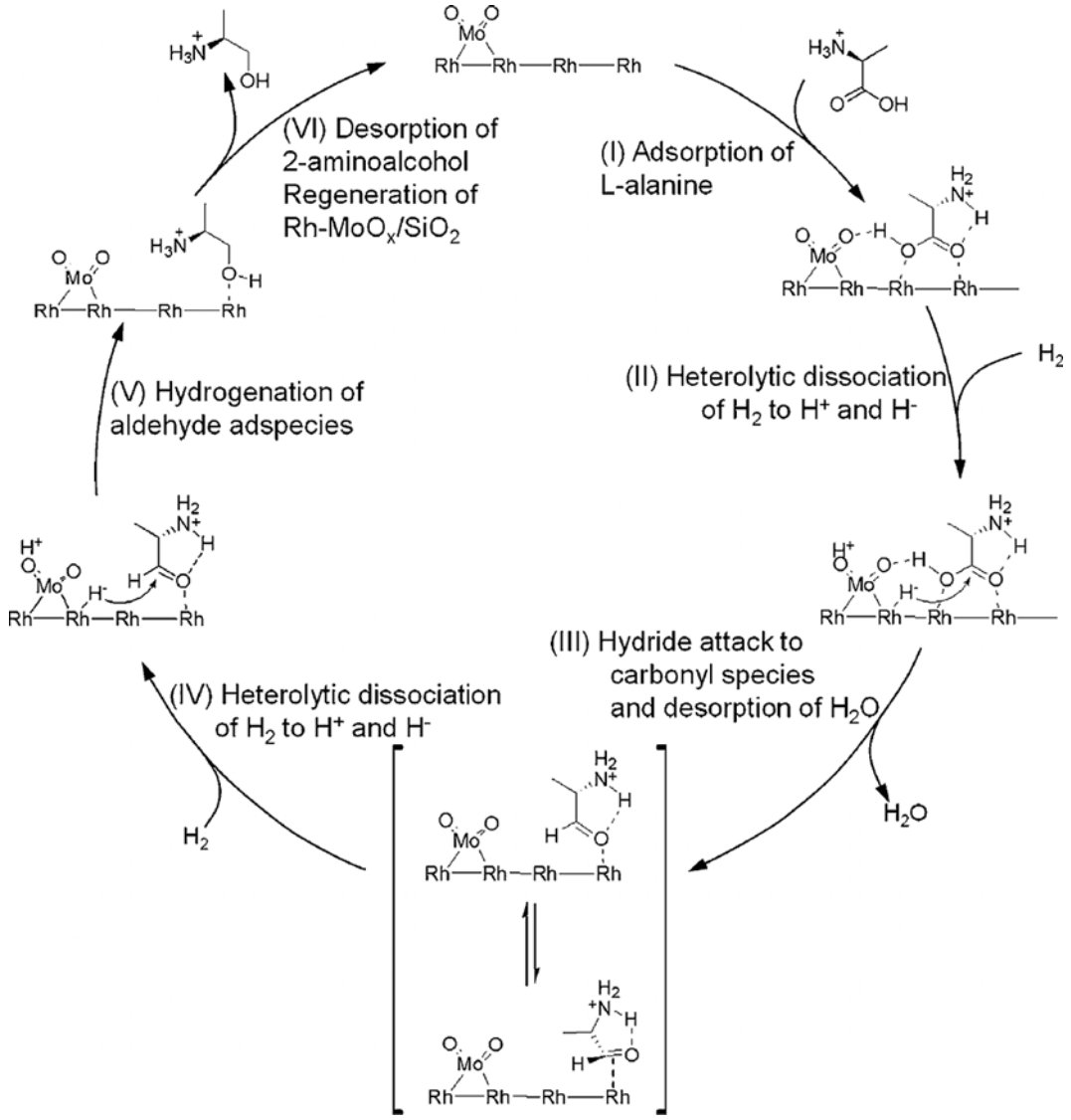


**Fig. 9.** Reaction mechanism for hydrogenation of L-alanine to L-alaninol over Rh–$MoO_x/SiO_2$ proposed by [19]. Reproduced with permission from Tamura et al. [19], *Chem. Eur. J.*; published by WILEY-VCH Verlag GmbH & Co. KGaA, 2015.

But on the other hand, a study by Kaku *et al.* [107] finds the traditional route of alcohol formation via acyl intermediates in the hydrogenation of L-proline using a Pt–$MoO_x/Al_2O_3$ catalyst. This makes comparisons with the study by Tamura *et al.* [19] difficult, as two different amino acids (L-alanine vs. L-proline) and different catalysts were used, with the only common element being the $MoO_x$ [107]. In addition, the study investigated the mechanisms of other catalysts, including Rh–$MoO_x/Al_2O_3$ [107]. However, here too, differences in the support materials used make a direct comparison difficult [107]. To clarify, it was also found that the performance of Rh–$MoO_x/Al_2O_3$ was inferior to that of Pt–$MoO_x/Al_2O_3$, which led to its removal from the study as the best catalyst for this specific reaction [107].

Further, kinetic evaluations conducted on the bimetallic catalyst Rh–$MoO_x/SiO_2$ for further explored the effects of second metal where a simple Arrhenius plot was used to determine the activation energy for the Rh–$MoO_x/SiO_2$ (45 kJ $mol^{-1}$) which was lower than that for the monometallic $Rh/SiO_2$ catalyst (54 kJ $mol^{-1}$) [19,80]. This reduction in activation energy due to the addition of $MoO_x$ indicates faster catalytic hydrogenation. When comparing Rh-based catalysts (mono- and bimetallic) with Ru/C catalysts, the Rh–$MoO_x/SiO_2$ catalyst showed much-improved performance with activation energies between 45–54 kJ $mol^{-1}$, compared to the higher activation energies of 81–88 kJ $mol^{-1}$ reported for Ru/C in the hydrogenation of L-alanine to L-alaninol [19,81,96].

Lastly, the reaction orders observed for both catalysts (Rh–$MoO_x/SiO_2$ and $Rh/SiO_2$) ranged from zero (Rh–$MoO_x/SiO_2$) to first order ($Rh/SiO_2$), consistent with previous studies [81,96] and aligning with the generally observed first-order kinetics for hydrogenation reactions [19]. These findings underscore the critical role of the second metal, $MoO_x$, in enhancing catalytic efficiency and selectivity in the hydrogenation of amino acids to amino alcohols.

Building on the fundamental understanding of hydrogenation mechanisms, we must also explore the decarboxylation of amino acids conversion, which also plays a crucial role in the production of N-chemicals such as the above-discussed diamines. While hydrogenation converts amino acids to produce amino alcohols, decarboxylation removes $CO_2$, facilitating the formation of other valuable compounds such as diamines. Both processes are influenced by similar kinetic parameters and reaction conditions, such as temperature and pH as presented, which affect the stability of intermediates and drive the reaction pathways. By studying both mechanisms, we can optimize catalytic systems for more efficient production of above- described N-chemicals from amino acids.

### 5.2. *Decarboxylation mechanism and kinetic*

The mechanistic investigation into the decarboxylation of amino acids such as L-lysine to produce diamines like cadaverine (see Fig. 6C) was proposed on the fundamental understanding of the hydrogenation which revealed some interesting findings about the intermediate steps and catalytic behaviour. Initially, no aldehyde intermediate, which is typical in the reduction of carboxylic acids to alcohols, was detected [97]. However, subsequent analysis confirmed its rapid conversion to amino alcohol (e.g., L-lysinol) [97]. This observation was consistent with mechanisms proposed for other amino acids with aliphatic side chains (e.g., L-lysine), as noted by [97]. Further investigation of L-lysine decarboxylation highlighted two key points [99]:

I.) Dimeric Pair Formation: The formation of "self-associate" dimeric pairs between the carboxyl groups of two L-lysine molecules was observed, which can slow down the catalytic conversion process. This intermolecular interaction suggests a potential rate-limiting step in the reaction mechanism.

II.) CO Hydrogenation to Methane: Carbon monoxide (CO), generated during the decarboxylation process, is hydrogenated on the ruthenium (Ru) active sites to methane ($CH_4$). This was later examined in detail by [105] and further supported by [93,99]. Investigations using CO adsorption studies on Ru active sites found two types of adsorption: bridge and linear. Bridge-type CO adsorption facilitated rapid hydrogenation to $CH_4$, clearing the active sites quickly, whereas linear-type CO adsorption exhibited stronger binding, thereby slowing down the catalytic conversion due to the CO's stronger interaction with the surface [102]. Furthermore, another example of such phenomena can also be observed for the hydrogenation of amino acids to amino alcohols, specifically L-proline to L-prolinol, where Pt-based catalyst (Pt–$MoO_x/Al_2O_3$) was used, showing quite a low yield of 48 %-59 %, which we suspect could be a result of such phenomena [107].

Further details of the decarboxylation mechanism of L-lysine to cadaverine were proposed by Ma *et al.* [93] see Fig. 10) using a bimetallic Ru–Mn/Beta catalyst and providing new information regarding the effect of the second metal on the catalyst. The excellent catalytic performance was attributed to the synergy between $RuO_2$ and oxygen vacancies, where L-lysine predominantly adsorbs onto the oxygen vacancies [93]. The mechanism begins with the formation of methyl species ($RCH_2O$–Mn), which then reacts with Ru–H species to produce L-lysinol, the amino alcohol of L-lysine [93]. Subsequent dehydration of L-lysinol leads to the formation of cadaverine [93]. Finally, during the literature review, it became evident that the only decarboxylation mechanism was investigated for the conversion of L-lysine and no mechanism was reported to N-chemicals such as ε-caprolactam. This highlights a significant gap in the research and presents a considerable opportunity for further exploration in this area. However, the mechanism for the removal of the amino group, known as hydrodenitrogenation (HDN), is listed in the literature [114,115] but was not explored for the use in the amino acids to the above-mentioned N-chemicals.

Further studies on the decarboxylation of other amino acids, such as (pyro)glutamic acid) to (N-butyl-)2-pyrrolidone [62,105], demonstrated that monometallic $Pd/Al_2O_3$ catalyst outperformed in terms of yield under similar reaction conditions (250 °C, water, nitrogen gas). This suggests that the presence of amino group may pose a challenge in decarboxylation reactions, potentially affecting the conversion of amino acids to amines or lactams, even though this effect was not observed in all studies [93,97,99].

This behaviour might be linked to the proximity of the carboxylic group to the amine group, which could hinder $CO_2$ removal. For example, in reactions involving L-proline, the cyclic structure might lead to easier decarboxylation to pyrrolidone despite the presence of the amine group. Notably, a bimetallic Pd–Pb/$ZrO_2$ catalyst was effective in overcoming this issue. Similarly, in the decarboxylation of L-lysine, the absence of adverse effects from the amino group's proximity to the carboxylic group could be attributed to the use of the Ru-Mn/Beta catalyst [93] and acidic conditions [99], both of which could mitigate potential negative interactions. Alternatively, the effects may have been negligible and thus overlooked in some studies [103].

These results illustrate the complex interplay of catalyst, interactions between intermediates and reaction conditions that influence the efficiency of amino acid decarboxylation. Importantly, both hydrogenation and decarboxylation are connected, as discussed above, and represent two primary mechanisms for converting amino acids into valuable N-chemicals. Hydrogenation processes, in which amino acids are converted to amino alcohols, provide fundamental insights into the kinetic parameters that also apply to decarboxylation, in which the removal of $CO_2$ is essential. For other reactions, such as deamination, however, there is a lack of comprehensive knowledge about the mechanism and kinetic evaluation compared to hydrogenation and decarboxylation. Understanding these two processes is therefore crucial for optimising catalyst design and reaction conditions to improve yield and target specific N-chemicals from amino acids, but other reactions, such as deamination, would also be beneficial.

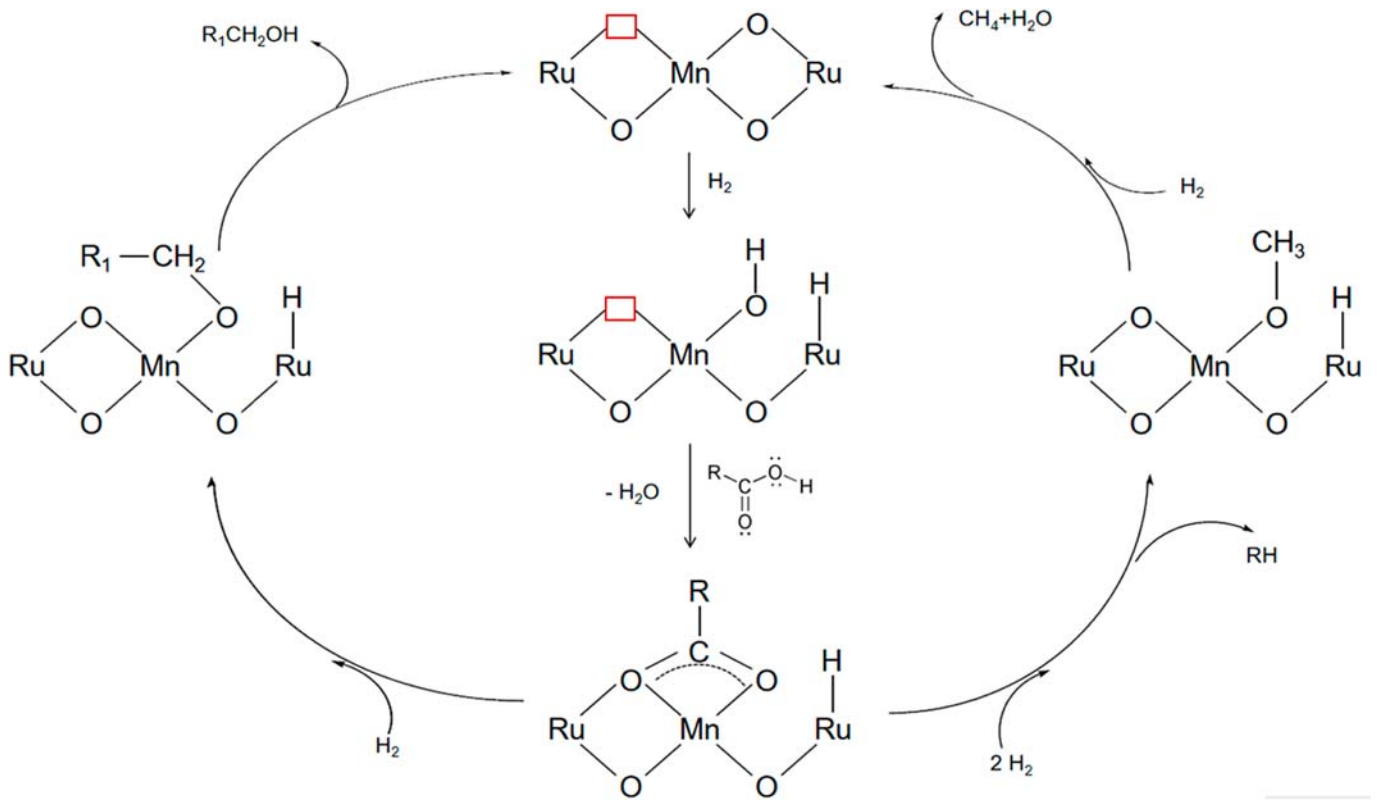


**Fig. 10.** Decarboxylation mechanism over a bimetallic catalyst for L-lysine to cadaverine. Reprinted (adapted) with permission from [93]. Copyright © 2021 American Chemical Society.

## 6. Conclusion

The review highlights the potential of nitrogen-rich biomass, such as algae and protein-derived materials, for sustainable production of nitrogen-containing chemicals via chemo-catalytic pathways. This approach promotes environmentally friendly processes, reducing reliance on fossil fuels and supports a bio-based economy. Algae, with their widespread availability, rapid growth, and high protein content, emerge as a particularly promising source of amino acids for producing valuable N-chemicals, including amino alcohols, lactams and diamines.

Research has shown that Ru-based catalysts are particularly effective for the hydrogenation and decarboxylation of amino acids, such as L-alanine, especially when supported on carbon. Furthermore, some studies have investigated the addition of secondary metals or metal oxides, such as Re or $Re_2O_7$, to enhance catalytic performance in hydrogenation targeting amino alcohols like L-alaninol. Notably, Ru on carbon generally exhibits the highest yields and selectivities, often exceeding 50 %.

But on the other hand, other noble metals such as Rh, Pt, Pd, and Ir, when supported on various supports, whether used as monometallic or bimetallic systems, achieve comparable or even superior results. However, direct comparisons among these catalysts remain challenging due to the diversity of reactions studied. For instance, the hydrogenation of L-alanine to L-alaninol using Rh–$MoO_x/SiO_2$ yields approximately 90 %, which is similar to the results obtained with Ru/C. Additionally, Ni-based and Cu-based catalysts supported on complex supports have also proven as effective catalysts for hydrogenating amino acids like L-phenylalanine to their corresponding amino alcohols like L-phenylalaninol, achieving yields around 90 % as well.

Additionally, other reactions, such as hydrodeoxygenation or decarboxylation, aim to produce higher carbon-number diamines, including cadaverine from L-lysine and targeted lactams like 2-pyrrolidone from glutamic acid. The yields for glutamic acid conversion to 2-pyrrolidone typically range from 51 % to 82 % when using Ru- or Pd-based catalysts. However, the conversion of L-lysine to cadaverine suffers from lower performance when utilizing Ru/C catalysts possessing yield of only around 50 %.

Moreover, the hydrodenitrogenation or deamination of L-lysine has been presented as promising, but it was less explored in the literature. When employed using Pt or Ir catalysts supported on carbon or zeolite resulted in poor yields, typically falling between 15 % and 65 %.

In general, these reactions are crucial for converting amino acids into the value-added above- mentioned and in the review discussed N-chemicals. Studies using kinetic modelling, such as the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model, have provided insights into the hydrogenation and decarboxylation mechanisms, emphasizing the importance of catalyst choice and reaction conditions. For instance, the addition of secondary metals, like Mo in Rh–$MoO_x/SiO_2$ catalysts, enhances performance by lowering activation energy and improving selectivity, highlighting the potential of bimetallic catalysts instead of monometallic such as Ru/C to be utilized in achieving efficient conversion.

Despite these advancements, significant challenges remain, particularly in integrating multiscale modelling to better understand reaction mechanisms and optimize catalyst design. Additionally, the decarboxylation of amino acids like L-lysine to produce diamines such as cadaverine presents opportunities for the synthesis of valuable chemical intermediates, though complexities in reaction mechanisms requiring further investigation. Future research should focus on developing novel catalysts with enhanced activity and selectivity, incorporating multiscale modelling for comprehensive mechanistic understanding, and exploring a wider range of amino acids from nitrogen-rich biomass sources. Process optimization and life cycle assessments will also be critical to evaluate the environmental impact and scalability of these technologies.

Nitrogen-rich biomass offers a promising pathway for sustainable N-

chemical production. Addressing existing research gaps and focusing on technological innovations will unlock the full potential of these resources, promoting a transition towards a more sustainable chemical industry.

## CRediT authorship contribution statement

**Rok Pogorevc:** Writing – original draft, Visualization, Validation, Investigation. **Brigita Hočevar:** Writing – review & editing, Supervision, Conceptualization. **Miha Grilc:** Writing – review & editing, Supervision, Conceptualization. **Blaž Likozar:** Writing – review & editing, Supervision, Resources, Conceptualization.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Data availability

Data will be made available on request.

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