

# Catalytic conversion of biomass-derived compounds to various amino acids: status and perspectives

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**Abstract** Amino acids are important nitrogen-containing chemicals that have a variety of applications. Currently, fermentation is the widely employed method to produce amino acids; however, the products are mostly limited to natural amino acids in the L-configuration. Catalytic synthesis is an alternative approach for the synthesis of amino acids with different types and configurations, where the use of renewable biomass-based feedstocks is highly attractive. To date, several lignocellulose and triacylglycerol-derived intermediates, typically  $\alpha$ -keto acids and  $\alpha$ -hydroxyl acids, have been transformed into amino acids via the amination reaction in the presence of additional nitrogen sources (i.e.,  $\text{NH}_3 \cdot \text{H}_2\text{O}$ ). Making full use of inherent nitrogen in biomass (i.e., chitin and protein) to produce amino acids avoids the use of extra nitrogen sources and meets the requirements of green chemistry, which is attracting increasing attention. In this review, we summarize different chemical-catalytic systems for the transformation of biomass to amino acids. An outlook on the challenges and opportunities for more effective production of amino acids from biomass by catalytic methods is provided.

**Keywords** biomass, amino acids, chitin, nitrogen-containing compounds, lignocellulose

## 1 Introduction

Amino acids are fundamental building blocks of proteins

Received June 23, 2022; accepted September 7, 2022

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and play a crucial role in life forms. Amino acids are important nitrogen-containing chemicals that face substantial global demand. They have been widely used in the field of pharmaceuticals, food, animal nutrients, cosmetics, etc. [1]. Currently, amino acids are being mainly produced on a large scale by microbial fermentation processes employing low-priced carbohydrates (i.e., starch, crude sugar, and molasses) and their derivatives as substrates [1,2]. Despite economic and environmental advantages, the biosynthesis of some amino acids by fermentation still suffers from several drawbacks, such as limited product scope (natural amino acids in L-configuration in most cases), strict operating conditions, and energy-intensive separation processes [3,4].

The catalytic production of amino acids is an alternative to their biosynthesis. The Strecker reaction is a classical method employed for the synthesis of amino acids starting from formaldehyde, cyanide, and ammonium salts [5], as shown in Scheme 1. The use of highly toxic formaldehyde and cyanide on a large scale might cause serious environmental and health problems, limiting the application of the Strecker reaction. As shown in Scheme 1, another typical method is Petasis synthesis for protected amino acids employing non-toxic boronic compounds as nucleophilic species [5]. In comparison with the Strecker reaction, Petasis synthesis can overcome some disadvantages by using more green and stable reagents. Although Petasis synthesis is promising, with the increasing demand of various amino acids, developing novel technologies for the green production is challenging and calls for further research efforts.

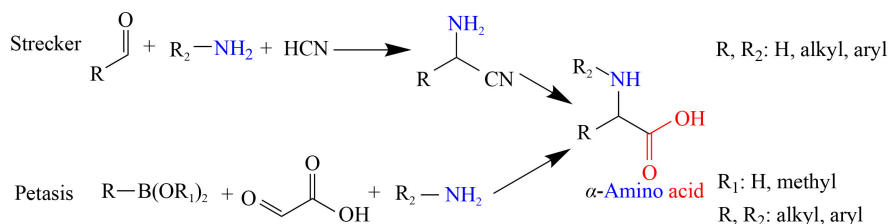
Recently, the catalytic production of amino acids from abundant and renewable biomass has attracted significant

attention [6,7]. As shown in Scheme 2, several derivatives of lignocellulose, triacylglycerol, and chitin have been used as substrates. When lignocellulose or triacylglycerol-derived compounds (typically,  $\alpha$ -keto acids,  $\alpha$ -hydroxyl acids, and glycerol) are used, additional nitrogen sources are needed for the amination of substrates to amino acids. In contrast, due to the existence of bio-fixed nitrogen, the synthesis of amino acids from chitin and proteins does not require additional nitrogen sources, which is a more promising strategy in terms of the energy-intensive ammonia synthesis. Previously, some reviews summarized amino acid production via biological pathways [2,4] and catalytic synthesis of organonitrogen chemicals from biomass-based feedstock [8]. Nonetheless, to the best of our knowledge, there has been no review dedicated to amino acid synthesis from renewable organic carbon sources via chemical pathways. Herein, we systematically summarized the advances in the catalytic synthesis of amino acids from biomass-based chemicals, in which different systems (substrates, catalysts, mechanism, etc.) were discussed.

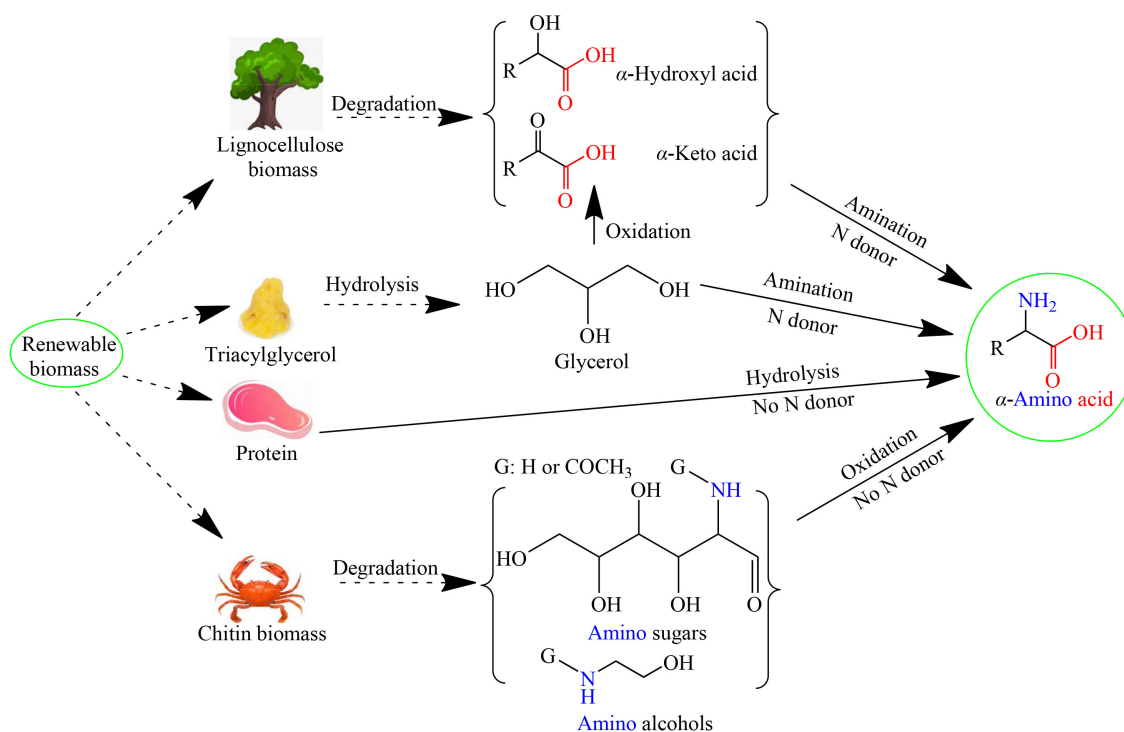
## 2 Conversion of lignocellulose or triacylglycerol biomass to amino acids

### 2.1 Conversion of lignocellulose or triacylglycerol biomass to intermediates for amino acid synthesis

Lignin, cellulose, and hemicellulose are typical biomass components. The conversion of lignocellulose to fine chemicals, fuels, and materials has been widely studied [9–12]. Various  $\alpha$ -hydroxyl acids, like lactic acid [13,14], glycolic acid [15–17], furylglycolic acid [18], and  $\alpha$ -hydroxyglutaric acid [19], are valuable compounds and have been produced via the degradation of lignocellulose. Among these, lactic acid has been extensively investigated. Various carbohydrates, such as glucose, fructose, xylose, and dihydroxyacetone, have been used for the preparation of lactic acid. Because the transformation of carbohydrates to lactic acid usually involves two key steps including isomerization and retro-aldol reactions, various homogeneous/heterogeneous acid



**Scheme 1** Production of amino acids via Strecker and Petasis reaction.

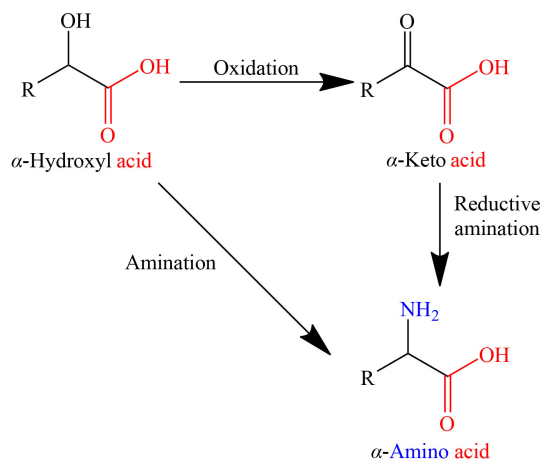


**Scheme 2** Overview of main chemical methods for production of amino acids from different biomass-based intermediates.

or base catalysts have been reported for these conversions [20]. To date, some encouraging chemo-catalytic systems for the production of lactic acid from biomass sugars have been reported. For example, Cao et al. [21] prepared an N-TiO<sub>2</sub> photothermal catalyst that could catalyze conversion of fructose, glucose, arabinose, and xylose into lactic acid, affording 93%, 85%, 96%, and 88% yields, respectively.

Triacylglycerol is another important biomass component and exists in both plants and animals. Glycerol can be produced by the hydrolysis of triacylglycerol. The direct conversion of glycerol to alanine has been reported [22]. Furthermore, the selective synthesis of lactic and glycolic acid can be achieved by regulating the competitive reaction pathways [23].

The product of  $\alpha$ -keto acids can be obtained by the simple oxidation of hydroxyl groups in  $\alpha$ -hydroxyl acids to carbonyl groups. As shown in Scheme 3, both  $\alpha$ -keto acids and  $\alpha$ -hydroxyl acids are potential substrates for the synthesis of corresponding amino acids by amination. Recent advances in this area will be discussed.



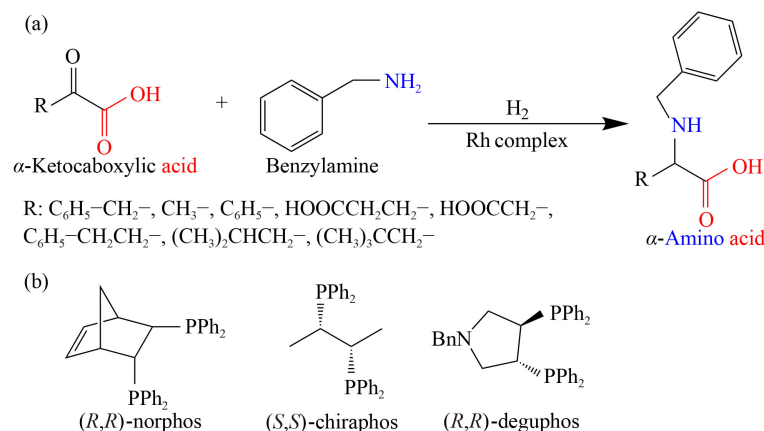
**Scheme 3** Conversion of  $\alpha$ -keto acids and  $\alpha$ -hydroxyl acids to amino acids.

## 2.2 Conversion of $\alpha$ -keto acids and their derivatives

### 2.2.1 Traditional thermocatalysis

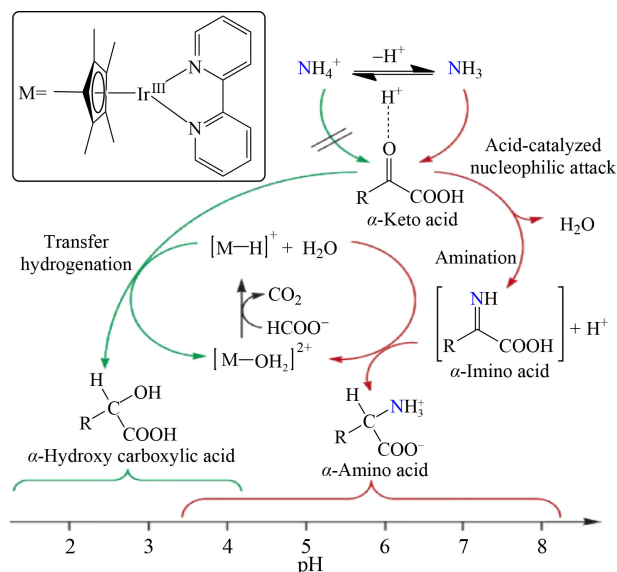
#### 2.2.1.1 Precious metal-based catalysts

Several Rh, Ir, and Pd-based catalysts have been used for the reductive amination of  $\alpha$ -keto acids to amino acids. Kitamura et al. [24] reported an efficient [RhCp\*Cl<sub>2</sub>]<sub>2</sub> complex for the reductive amination of various ketones under mild conditions in the presence of HCOONH<sub>4</sub>, affording corresponding primary amines in satisfactory yields. Herein, HCOONH<sub>4</sub> acted as both a hydrogen and nitrogen resource. This method was also employed for the catalytic reductive amination of  $\alpha$ -keto acids to corresponding  $\alpha$ -amino acids in methanol with good yields. Typically, a high phenylglycine yield of 91% was obtained from phenylglyoxylic acid at 50 °C for 1.5 h. Notably, the procedure for purification of these  $\alpha$ -amino acids was simple. Due to poor solubility of the product in methanol, it can usually be separated from reaction mixtures by filtration. Kadyrov et al. [25] reported that Rh-based catalysts were used for the reductive amination of biomass-derived  $\alpha$ -keto acids (Scheme 4). As shown in Scheme 4(a), benzylamine was used as nitrogen resource, as the benzyl group is a suitable protecting group and can be easily removed. The catalysts were synthesized *in situ* via the reaction of 96 chiral ligands with [Rh(COD)<sub>2</sub>]BF<sub>4</sub> and [Rh(COD)Cl]<sub>2</sub>, respectively. High-throughput screening showed that the chiral ligand has a remarkable effect on the catalytic performance. Among others, (*R,R*)-norphos, (*S,S*)-chiraphos, and (*R,R*)-deguphos were superior, possibly owing to their five-membered structure bearing diphenylphosphino groups, presented in Scheme 4(b). Taking phenylpyruvic acid as an example, the catalysts based on these three ligands had both high yields ( $\geq 98\%$ ) and *ee* values ( $\geq 91\%$ ). Thereby, several natural amino acids, including glutamic acid, leucine, and alanine in protected form, have been produced with high stereoselectivity.



**Scheme 4** (a) Conversion of  $\alpha$ -keto acids to amino acids over Rh-based catalysts. (b) Structures of (*R,R*)-norphos, (*S,S*)-chiraphos, and (*R,R*)-deguphos. Reprinted with permission from Ref. [25], copyright 2003, American Chemical Society.

Ir-based catalysts have likewise shown promising activity for this reaction. Unlike previous catalytic systems with organic solvents as reaction medium, Ogo et al. [26] achieved reductive amination in aqueous  $\text{NH}_3$  and  $\text{HCOOH}/\text{HCOONa}$  over Ir complexes  $[\text{Cp}^*\text{Ir}^{\text{III}}(\text{bpy})\text{H}]n(\text{X})$ , where  $\text{X} = \text{SO}_4$  ( $n = 2$ ) or  $\text{PF}_6$  ( $n = 1$ ),  $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$ ,  $\text{bpy} = 2,2'$ -bipyridine. The use of green solvent (i.e., water) is attractive. As proposed in Scheme 5, the reductive amination starts from a nucleophilic attack of  $\text{NH}_3$  to the carbonyl carbon catalyzed by protons in acidic medium, yielding the  $\alpha$ -imino acid as a key intermediate. The further reduction of  $\text{C}=\text{N}$  in  $\alpha$ -imino acid yields the  $\alpha$ -amino acid. Therefore, the reductive amination requires acid-stable catalysts. Meanwhile, an acidic environment facilitates the protonation of  $\text{NH}_3$  to form  $\text{NH}_4^+$  that cannot act as the nitrogen donor, where  $\alpha$ -keto acids are hydrogenated to  $\alpha$ -hydroxyl acids. The selective conversion of  $\alpha$ -keto acids to amino acids has been achieved by using these acid-stable Ir-based catalysts and adjusting the pH value of reaction medium, while the reduction of  $\alpha$ -keto acids to  $\alpha$ -hydroxyl acids is inhibited as well. Recently, Nguyen et al. [27] developed a novel system for amino acid synthesis over  $[\text{Cp}^*\text{Ir}(\text{N-phenyl-2-pyridinecarboxamidate})\text{Cl}]$  in methanol, where  $\text{HCOONH}_4$  provided both nitrogen and hydrogen. After the reaction at 37 °C for 6 h, several typical amino acids, including glycine, alanine, and tyrosine, were obtained in good isolated yields above 90%. Under the same conditions, the yields of phenylalanine (62%) and DOPA (82%) were relatively low due to the loss during product recovery. Consistent with previous reports [26], the reductive amination of  $\alpha$ -keto acids in an aqueous medium with low



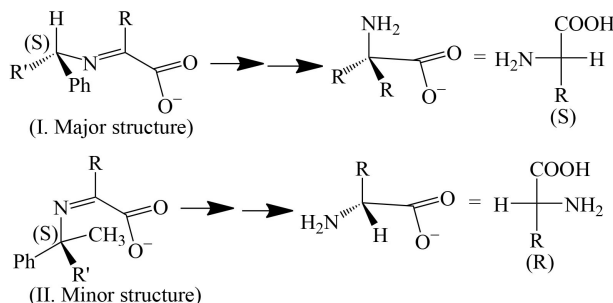
**Scheme 5** pH-dependent reductive amination of  $\alpha$ -keto acids in the presence of  $\text{NH}_3$  and  $\text{HCOO}^-$  over Ir complexes. Reprinted with permission from Ref. [26], copyright 2004, American Chemical Society.

pH value significantly promoted the formation of  $\alpha$ -hydroxyl acids, which supported the dependence of product selectivity on proton concentration. However, it must be noted that the effect of the pH value on  $\alpha$ -keto acids conversion is complicated and requires further study. As a useful metal, the Ir-based catalyst has been used for reductive amination of ketone, aldehyde, and  $\alpha$ -keto acids to corresponding nitrogen-containing compounds [28].

In addition to Rh and Ir, Pd-based catalysts have also been demonstrated for the synthesis of amino acids from  $\alpha$ -keto acids [29,30]. Chang et al. [30] reported that the supported Pd nanoparticles have good catalytic performance for the reductive amination of  $\alpha$ -keto acids using (S)-(-)- $\alpha$ -methylbenzylamine as nitrogen resource, affording high enantioselectivity. Under optimized conditions, 81 and 88 *ee* % were obtained over 10% Pd/SBA-15 and Pd/NaY, respectively. For both Pd/SBA-15 and Pd/NaY, the highest *ee* % was achieved at  $\text{H}_2$  pressure of  $3.5455 \times 10^5$  Pa. In addition to  $\text{H}_2$  pressure, another key parameter was the Pd metal size. The authors proposed that Pd catalysts with larger crystallite size had regularly-arranged metal atoms on the catalyst surface, providing an appropriate environment for enantio-differentiation during the hydrogenation step and producing high optical yields. Taking pyruvic acid as an example, as shown in Scheme 6, Structure I was the major structure during the reaction, resulting in the highly selective synthesis of (S)-alanine.

### 2.2.1.2 Non-precious metal-based catalysts

Compared to precious metals, the use of non-precious metal catalysts is significantly more attractive, with limited examples so far. Chan et al. [31] reported the effective reductive amination of  $\alpha$ -keto acids to desired amino acids over the commercial Raney nickel catalyst.  $\text{H}_2$  was employed as the hydrogen donor, while both ammonia gas and aqueous ammonia act as aminating agents in methanol. Using sodium  $\beta$ -phenylpyruvate as substrate, a high yield of phenylalanine above 98% was achieved in the presence of aqueous ammonia under mild conditions (50 °C, 20 h, 200 psig  $\text{H}_2$ ). Considering the relatively poor stability of  $\beta$ -phenylpyruvic acid, the satisfactory



**Scheme 6** Conformation of substrates. Reprinted with permission from Ref. [30], copyright 2003, Elsevier B.V.

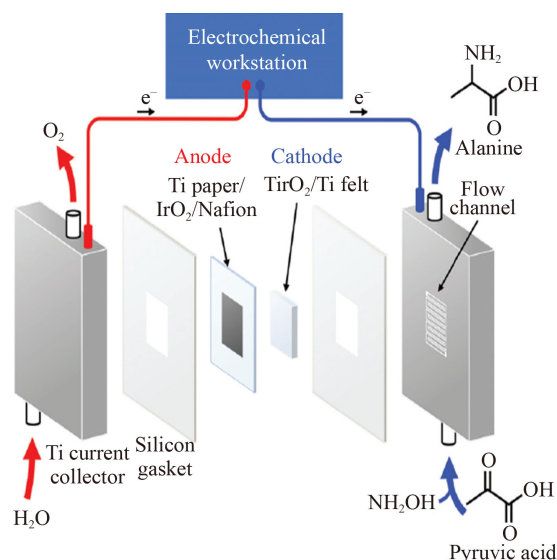


yield of phenylalanine might be ascribed to the rapid trapping of  $\beta$ -phenylpyruvic acid by ammonia, which can effectively inhibit the decomposition of  $\beta$ -phenylpyruvic acid. When aqueous ammonia is used under the same condition, sodium  $\beta$ -phenylpyruvate, *p*-hydroxyphenylpyruvic acid, pyruvic acid, and benzoylformic acid were converted to their corresponding amino acids with good yields of  $\geq 97\%$ , indicating the promising potential of nickel catalysts. Unfortunately, to the best of our knowledge, there are no further reports on the progress of nickel-catalyzed reductive amination of  $\alpha$ -keto acids.

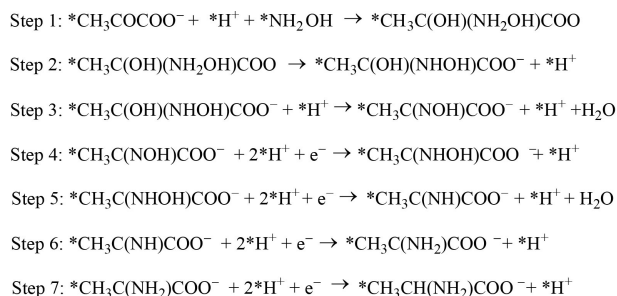
Another interesting case of iron oxyhydroxide was recently reported by Barge et al. [32]. They demonstrated that mixed-valence iron oxyhydroxides could drive reductive amination of pyruvate to form alanine, while pyruvate could also be reduced to lactate. The selectivity of products depended on the ratio of Fe(II) to Fe(III) in the iron hydroxide catalysts. Pure ferrous hydroxides could catalyze the reduction of pyruvate to lactate, but showed no activity for the alanine production, while ferric hydroxides exhibited no catalytic activity for both reductive amination and reduction of pyruvate. In fact, the partially oxidized state of the catalyst significantly promoted the formation of alanine, yielding the highest yield of alanine (ca. 70%) as well as ca. 30% lactate at 70 °C for 72 h when Fe(II)/Fe(III) ratio was 1:1. The need of mixed-valence indicates the synergistic effect of Fe(II) and Fe(III) components. Unfortunately, the catalysts are sensitive to oxygen, making the experimental results difficult to reproduce. Similarly to other systems [26], alkaline conditions significantly promote the formation of alanine, and neutral conditions only facilitate the synthesis of lactate. The development of stable and repeatable Fe-based catalysts is a promising strategy in view of the low price and abundance of the iron element on earth.

### 2.2.2 Electrocatalysis

Electrochemical hydrogenation of biomass-based compounds with water as the hydrogen donor has attracted significant attention owing to its mild reaction conditions and simplicity [33]. Fukushima et al. [34] demonstrated the electrocatalytic production of several amino acids from biomass-derived  $\alpha$ -keto acids on  $\text{TiO}_2/\text{Ti}$  mesh electrodes, affording Faradaic efficiencies of 77%–99% using  $\text{NH}_2\text{OH}$  as a nitrogen source. Compared to  $\text{NH}_3$  for pyruvic acid conversion,  $\text{NH}_2\text{OH}$  can significantly enhance the formation of amino acid and inhibit the reduction reaction. Nevertheless,  $\text{NH}_2\text{OH}$  has its shortcomings, including instability and toxicity. The authors developed a flow-type reactor named polymer electrolyte amino acid electrosynthesis cell (AAEC) for the continuous synthesis of alanine from pyruvic acid, achieving 89% conversion with 77% Faradaic efficiencies (Fig. 1). The same group [35] further investigated the reaction mechanism of



**Fig. 1** Electrosynthesis of alanine from pyruvic acid and  $\text{NH}_2\text{OH}$  using AAEC. Reprinted with permission from Ref. [34], copyright 2019, Royal Society of Chemistry.



**Scheme 7** Elemental reactions from pyruvic acid to alanine. Reprinted with permission from Ref. [35], copyright 2021, American Chemical Society.

alanine production using density functional theory, and several important findings were summarized as follows. As shown in Scheme 7, the formation of alanine consists of seven elementary reactions mainly described by proton transfer. The formation of the N–H bond from the oxime intermediate to alanine is the key step with the highest energy barrier. This step is mediated by a proton-coupled electron transfer reaction, resulting in lower activation energy. The  $\text{H}_2\text{O-TiO}_2$  interface enhances alanine formation for two main reasons. First, the protons bound to the surface oxygen of the  $\text{TiO}_2$  transfer to the acceptors with the assistance of the hydrogen bond network of water molecules in most steps. Furthermore, compared to water, pyruvic acid has stronger affinity with  $\text{TiO}_2$  surface, which facilitates electron transfer from  $\text{TiO}_2$  to pyruvic acid.

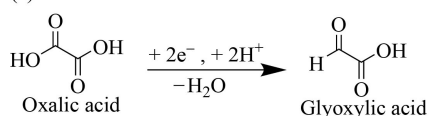
In addition to  $\alpha$ -keto acids, the Yamauchi group [36] likewise investigated the electrosynthesis of glycine from oxalic acid and  $\text{NH}_2\text{OH}$ . Oxalic acid is a typical dicarboxylic acid derived from the biomass [37]. As shown in

**Scheme 8**, oxalic acid is reduced to glyoxylic acid, an  $\alpha$ -keto acid, as an intermediate product. Further reductive amination of glyoxylic acid produces glycine. This work provides an example for amino acid preparation by using an upstream compound of  $\alpha$ -keto acid as substrate, and moderate Faradaic efficiency was obtained.

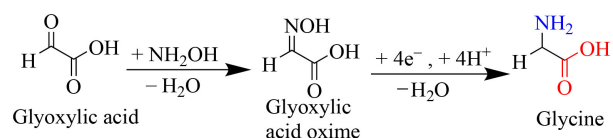
### 2.3 Conversion of $\alpha$ -hydroxyl acids intermediates

The transformation of  $\alpha$ -hydroxyl acids is another method to produce amino acids, which usually requires relatively harsh reaction conditions [38–41]. The Yan's group [38] reported a heterogeneously catalytic conversion of  $\alpha$ -hydroxyl acids derived from lignocellulosic biomass to

(a) The formation of  $\alpha$ -keto acid

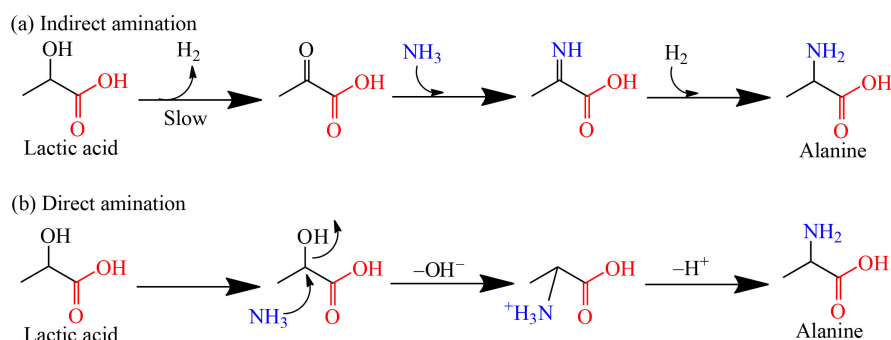


(b) Reductive amination of  $\alpha$ -keto acid

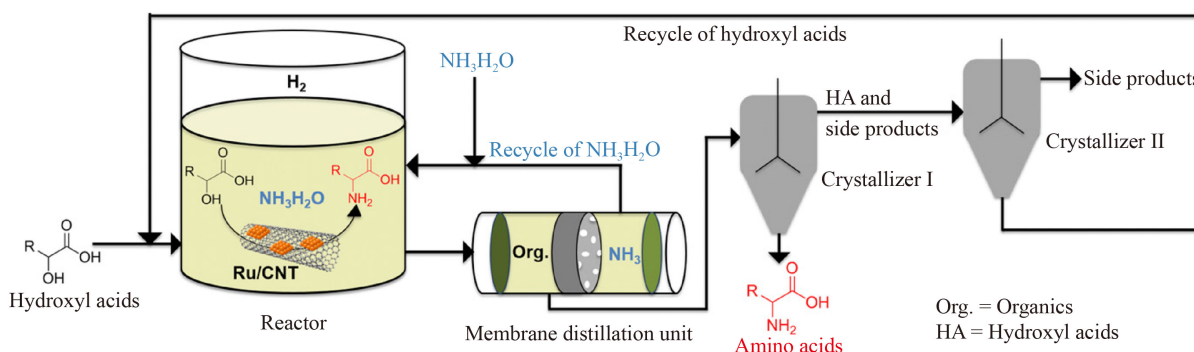


**Scheme 8** Reaction route for glycine formation from oxalic acid. Reprinted with permission from Ref. [36], copyright 2021, Springer.

the desired amino acids including alanine, leucine, valine, aspartic acid, and phenylalanine with moderate yields, where ammonia and  $\text{H}_2$  were used. As shown in **Scheme 9**, there are two possible mechanisms for alanine formation from lactic acid. In comparison with lactic acid, the treatment of  $\alpha$ -hydroxyl isobutyric acid without an  $\alpha$ -H under various conditions generated no corresponding amino acid, suggesting that the indirect route is dominant. Some recent investigations further supported the dehydrogenation–amination–hydrogenation pathway [41,42]. The dehydrogenation of hydroxyl groups generates  $\alpha$ -keto acid intermediates first, which is a slow process and considered as the rate-determining step. Compared to Pd, Pt, Rh, and Ir, the Ru nanoparticles supported on carbon nanotubes (Ru/CNT) showed better amino acid formation performance owing to the significant enhancing effect of Ru for dehydrogenation in the presence of  $\text{NH}_3$ . The use of Ru/CNT modified with 10 wt % Ni slightly increased the yields of amino acids. A two-step chemical process for the conversion of glucose to alanine with lactic acid as the intermediate produced a satisfactory overall yield of 43%, which is comparable with that of well-developed biotechnology. Moreover, the product purification from ammonia solution by membrane distillation was proposed, as shown in **Fig. 2**. This study offers a novel and valuable strategy for the production of amino acids from lignocellulosic biomass-derived compounds. Subsequently, Xie et al. [39] found that the use of Ru/N-CNTs promoted amino acid production and inhibited the



**Scheme 9** Two possible reaction pathways for amination of lactic acid to alanine. Reprinted with permission from Ref. [38], copyright 2018, National Academy of Sciences.

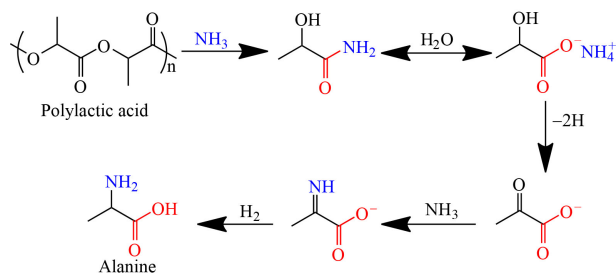


**Fig. 2** Conceptual process diagram for synthesis and purification of amino acids. Reprinted with permission from Ref. [38], copyright 2018, National Academy of Sciences.

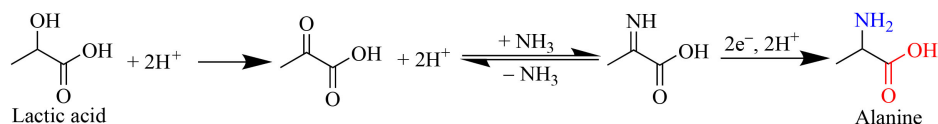
amide formation from  $\alpha$ -hydroxyl acids under milder conditions (180 °C vs 220 °C), where N-CNTs represents nitrogen-doped CNTs. The nitrogen-containing species facilitated the dispersion of Ru nanoparticles on N-CNTs and strengthened the interaction between active Ru nanoparticles and supports. Moreover, the nitrogen-containing basic sites favored the adsorption of acidic reactants, which also promoted the formation of amino acids.

As an important  $\alpha$ -hydroxyl acid, lactic acid has been regarded as a promising monomer to produce biodegradable plastic polylactic. In comparison with the natural carbon-emitting degradation process, the selective upcycling of waste polylactic plastic into value-added products is highly desirable. Tian et al. [42] developed a simple method for “one-pot” conversion of polylactic acid over Ru/TiO<sub>2</sub> in ammonia solution at 140 °C, affording a 77% yield of alanine. Unlike lactic acid as a substrate [38–41], no additional hydrogen resource was required. Both lactamide and ammonium lactate were key intermediates for alanine formation, as shown in Scheme 10. The reuse of byproducts like lactamide and ammonium lactate as a reactant after separating alanine enhanced the overall selectivity of alanine to 94%.

In addition to traditional thermocatalysis, photocatalysis has also been applied in amino acid synthesis from  $\alpha$ -hydroxyl acids [43,44]. For example, Song et al. [43] reported the visible-light-driven amination of  $\alpha$ -hydroxyl acids at 50 °C using NH<sub>3</sub> as nitrogen resource. Among the commercial and homemade CdS materials, the self-prepared ultrathin CdS nanosheets exhibited the best catalytic performance and good stability for the synthesis of alanine from lactic acid with a productivity up to 10.5 mmol·g<sup>-1</sup>·h<sup>-1</sup>. There are two main reasons for its superior activity. First, it could enhance the formation of



**Scheme 10** Proposed reaction mechanism of polylactic acid amination on a Ru/TiO<sub>2</sub> catalyst in ammonia solution. Reprinted with permission from Ref. [42], copyright 2021, American Chemical Society.



**Scheme 11** Reaction route for alanine formation from lactic acid. Reprinted with permission from Ref. [43], copyright 2020, Springer.

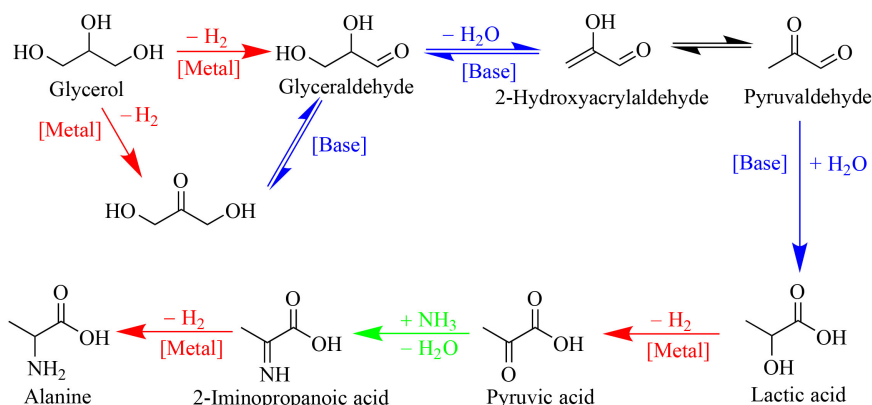
oxygen-centered radicals, which further promotes the dehydrogenation reaction to produce a pyruvic acid intermediate. Consistent with previous results [38], pyruvic acid generation is also identified as the rate-determining step. CdS nanosheets showed the poorest H<sub>2</sub> synthesis ability, which decreased the consumption of electrons and facilitated the amination of pyruvic acid to alanine, as shown in Scheme 11. In addition to alanine, several amino acids have been produced by this process, starting from corresponding  $\alpha$ -hydroxyl acids, and the one-pot conversion of glucose to alanine can be achieved in productivity of 0.34 mmol·g<sup>-1</sup>·h<sup>-1</sup>. Another example is that the use of Mo-doped In<sub>2</sub>O<sub>3</sub> yielded an 81% conversion of lactic acid with 91% selectivity of alanine under visible-light irradiation at 50 °C [44]. Despite the photocatalysis potential in the production of amino acids, successful cases are still limited.

## 2.4 Conversion of other nitrogen-free intermediates

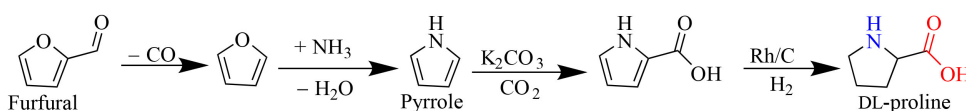
Taking advantage of similar structures, the production of amino acids from  $\alpha$ -keto acids or  $\alpha$ -hydroxyl acids requires the amination of carbonyl or hydroxyl groups with the retention of carboxyl groups. Starting from other substrates that do not contain amino and carboxyl groups, the synthesis of amino acids requires their simultaneous synthesis, which is typically difficult. Herein, we introduce two recently reported examples.

Glycerol is a low-cost and abundant biodiesel-derived compound [45,46]. Wang et al. [22] developed one-pot synthesis of alanine from glycerol via a lactic acid intermediate over a single Ru<sub>1</sub>Ni<sub>7</sub>/MgO catalyst with a yield of 43% in the presence of NaOH and H<sub>2</sub> in aqueous ammonia. As shown in Scheme 12, multiple steps including dehydrogenation, isomerization, amination, dehydration, and hydrogenation have been integrated in a single-step process with high yield of the desired product, which provides a successful case for the design of multifunctional catalysts (i.e., bimetallic catalyst) in biorefinery.

Furfural is a crucial platform compound produced from biomass [47]. Song et al. [48] reported the single-step conversion of furfural to pyrrole through tandem decarbonylation–amination reactions over Pd@S-1 combined with H-beta zeolite with a yield of 75%, as shown in Scheme 13. The carboxylation of pyrrole by K<sub>2</sub>CO<sub>3</sub> generated pyrrole-2-carboxylic acid with 63% yield, and the hydrogenation of pyrrole-2-carboxylic acid over Rh/C produced DL-proline in 98% yield. Notably, the DL-



**Scheme 12** Proposed reaction network for glycerol conversion. Reprinted with permission from Ref. [22], copyright 2020, Wiley.



**Scheme 13** Conversion of furfural to proline. Reprinted with permission from Ref. [48], copyright 2020, John Wiley and Sons Ltd.

proline isolated from reaction mixtures can be selectively converted into D-proline by treatment with *Escherichia coli*. By using both chemical and biologic methods, furfural was successfully transformed into valuable D-proline.

### 3 Conversion of nitrogen-containing biomass to amino acids

#### 3.1 Conversion of protein and derivatives

The hydrolysis of protein might produce a mixture of oligopeptides and various amino acids. In strongly acidic or alkaline medium, protein can be nearly completely hydrolyzed, whereas some amino acids would be degraded. The use of concentrated acid or base solution (i.e., 6 mol·L<sup>-1</sup> HCl or 5 mol·L<sup>-1</sup> NaOH) might cause numerous problems, such as the risk of acid/base leakage, strong corrosiveness to reactor, and salt waste generation upon neutralization. To date, protein hydrolysis has usually been applied as an analytical method [49].

#### 3.2 Conversion of chitin and its derivatives

Chitin containing about 7 wt % bio-fixed nitrogen is the second most abundant biopolymer after cellulose. Owing to the presence of organonitrogen, chitin is a promising raw material for the production of nitrogen-containing chemicals, such as amino sugars, amino alcohols, or heterocyclic compounds [50]. The deacetylation of chitin produces chitosan. N-acetyl glucosamine (NAG) and glucosamine (GlcN) are the main products obtained by the hydrolysis of chitin and chitosan, respectively. The corresponding amino acids can be prepared by the direct

oxidation of amino sugars or their analogues. Moreover, some precursors of small amino acids can be obtained via the C–C cleavage of amino sugars, which provides the possibility to produce other valuable amino acids in addition to amino sugar acids. The study of the synthesis of amino acids from chitin biomass has attracted significant attention [51–53]. Here, we briefly introduced the progress in this area.

##### 3.2.1 Amino sugar acid as product

In early investigations in 1915, yellow mercuric oxide was used as oxidizing agent to oxidize GlcN hydrochloride (GlcN-HCl) with a ca. 54% yield of glucosaminic acid (GlcNA) [54]. Wolfrom and Cron [55] prepared GlcNA from crab containing chitin with a yield of 62% by the sequential HCl-catalyzed chitin hydrolysis, GlcN-HCl purification, and GlcN-HCl oxidation by using half of the oxidant amount compared to the previous method [54]. Considering safety and oxidation efficiency, the use of toxic oxidants (i.e., yellow mercuric oxide) must be avoided as much as possible.

Several heterogeneous catalysts for green catalytic oxidation of GlcN by O<sub>2</sub> have been developed. Both catalysts (supports and supported components) and the reaction medium significantly affect the catalytic performance. Gu and Xia [56] reported a 70% isolated yield of GlcNA from GlcN-HCl over Pd-Bi/C under mild conditions (30 °C, 6 h), where nontoxic O<sub>2</sub> was used as the oxidant. The addition of bases (i.e., NaOH and KHCO<sub>3</sub>) was carried out to neutralize as-formed GlcNA. Notably, Pd-Bi/C still exhibited good activity after eight catalytic runs. Compared with the previous systems [54,55], green oxidant, environment-friendly procedures and reusable heterogeneous catalysts all indicate



encouraging progresses. Ohmi et al. [57] demonstrated that Au nanoparticles supported on basic supports (i.e., hydrotalcite and MgO) are promising catalysts for the oxidation of GlcN-HCl and its derivatives, and an 87%–99% yield of corresponding amino acids could be obtained under mild conditions (20–40 °C, 2–5 h, O<sub>2</sub> flow). The use of basic supports significantly enhanced the yield of amino acids and required no additional bases. Furthermore, Au/MgO showed stable catalytic performance for three successive runs, and they speculated the strong interaction between Au nanoparticles and MgO contributing to the stability of Au/MgO. Recently, Zheng et al. [58] demonstrated that Au/ZnO with average particle size of 1.5–2.5 nm could effectively catalyze oxidation of GlcN-HCl to GlcNA in an open beaker without any basic additive, producing a considerable yield of 85% at 35 °C for 2 h. Both the surface oxygen vacancies and smaller-sized Au nanoparticles on supports contributed to the high catalytic activity. The introduction of a strong base (i.e., NaOH) or oxidant (i.e., H<sub>2</sub>O<sub>2</sub>) could further facilitate GlcNA formation.

Considering the complex process of GlcN preparation, the direct conversion of chitosan to GlcNA is a more attractive option, which avoids the purification step. Dai et al. [59] investigated the feasibility for the synthesis of GlcNA from chitosan by using heterogeneous catalysts. As shown in Scheme 14, commercial Amberlyst-15 catalyzed the hydrolysis of chitosan sulfate with monomer/H<sub>2</sub>SO<sub>4</sub> ratio of 1:1, and the GlcN yield was 58%. After the removal of Amberlyst-15, the GlcNA yield of direct oxidation of hydrolysate over Au/MgO was only 17%, which could be ascribed to the catalyst poisoning caused by humin-like byproducts. Importantly, the GlcNA yield could be improved to 63% after selective removal of undesirable side-products by activated carbon. A total GlcNA yield of 35% was obtained from chitosan without purification of GlcN, but further improvement on

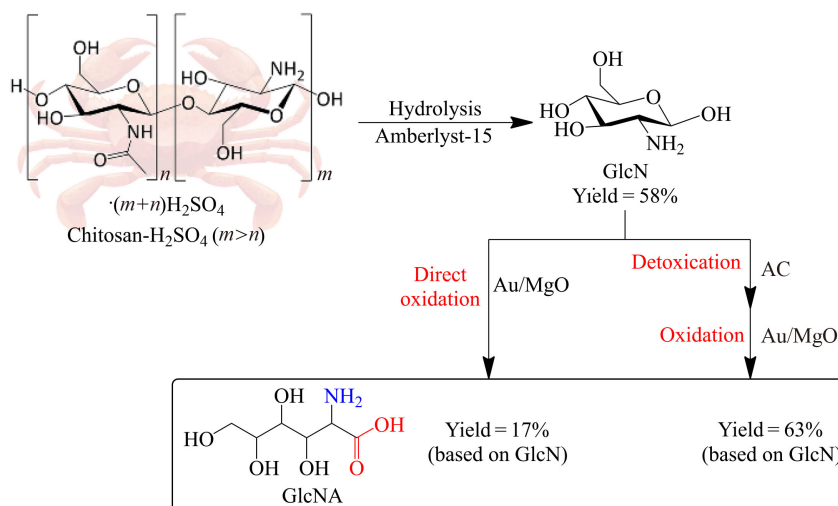
catalysts and catalytic systems is required to increase the yield of GlcNA.

### 3.2.2 Acetylglycine or glycine as product

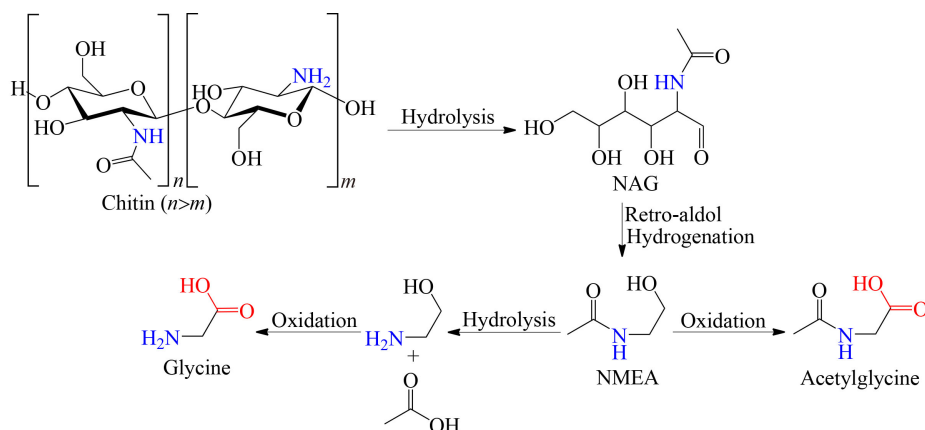
Some small nitrogen-containing chemicals have been obtained via C–C cleavage of amino sugars. For example, 2-acetamido-acetaldehyde, a product formed by the retro-aldol of NAG, can be further converted into *N*-acetylmonoethanolamine (NMEA) by hydrogenation. The hydrolysis products of NMEA are ethanolamine and acetic acid. These chitin-derived NMEA and ethanolamine are potential substrates for the synthesis of corresponding amino acids by oxidation of hydroxyl group to carboxyl group, as shown in Scheme 15.

Hu et al. [60] systematically investigated the preparation of amino acids from amino alcohols over a Ru-based complex in a strong alkaline medium with H<sub>2</sub>O as the oxygen donor and H<sub>2</sub> as a useful product, as shown in Scheme 16. Under optimized conditions, 99% glycine and 95% acetylglycine were obtained from ethanolamine and NMEA using 2 and 10 equivalent NaOH, respectively. This study proposed a general and efficient method for green oxidation of amino alcohols by H<sub>2</sub>O, but the stability and recyclability of the catalysts must be further investigated.

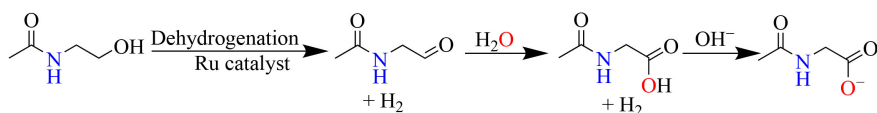
Techikawara et al. [61] prepared a 5 wt % Ru/C catalyst to convert NAG toward acetylglycine via an NMEA intermediate in the presence of NaHCO<sub>3</sub>. In the first step for the synthesis of NMEA, the direct hydrogenation of NAG to 2-acetamido-2-deoxysorbitol in H<sub>2</sub> atmosphere was the main side-reaction, and the formation of NMEA was inhibited. Only 29% yield of NMEA (based on N) was achieved under optimized conditions. In the second step, the highest yield of acetylglycine by the oxidation of NMEA over Ru/C in O<sub>2</sub> was 40%. Because the catalysts adsorbed undesirable



**Scheme 14** Protocol for catalytic conversion of chitosan to GlcNA. Reprinted with permission from Ref. [59], copyright 2019, American Chemical Society.



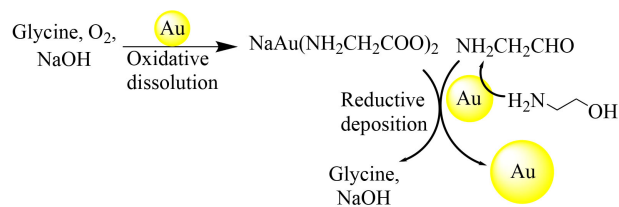
**Scheme 15** Conversion of chitin biomass to glycine and its derivatives.



**Scheme 16** Oxidation of NMEA by water under basic conditions.

products like humins, the catalytic activity gradually decreased.

Gold is another metal that has been widely applied in oxidation reactions [62]. Biella et al. [63] reported that the conversion of ethanolamine over Au/Al<sub>2</sub>O<sub>3</sub> was 23% under basic conditions at 70 °C, with low selectivity toward glycine due to the formation of dimers. Under the same conditions, Pd/C and Pt/C showed no activity for ethanolamine conversion, probably because of the irreversible adsorption of the amino group on supported Pd and Pt catalysts [62]. Villa et al. [64] further demonstrated that the facile coordination of amino groups in ethanolamine with the catalyst active site leads to a remarkable decrease of catalyst durability. To enhance the synthesis of glycine, Meng et al. [65] added polyvinyl alcohol (PVA) to fabricate a capping layer during catalyst preparation. The formed PVA capping layer inhibited the interaction of amino group with Au nanoparticles via desirable hydrogen bonds between the amino group of ethanolamine and hydroxyl group of PVA, which significantly enhanced the oxidation of ethanolamine with a 95% yield of glycine. The same group [66] found the aggregation of Au nanoparticles as the main reason for catalyst deactivation. As shown in Fig. 3, an oxidative dissolution-reductive deposition mechanism during ethanolamine oxidation was proposed, which might help us understand the deactivation mechanism of Au catalysts in oxidation reactions.



**Fig. 3** Proposed oxidative dissolution-reductive deposition mechanism of Au nanoparticles aggregation. Reprinted with permission from Ref. [66], copyright 2020, Elsevier.

processes of chemo-catalytic conversion of renewable biomass-derived feedstock to amino acids have attracted increasing attention. Nitrogen-free lignocellulose and triacylglycerol-derived chemicals, including  $\alpha$ -keto acids,  $\alpha$ -hydroxyl acids, glycerol and their derivatives, are potential substrates for the synthesis of amino acids via the amination step. The dehydrogenation of  $\alpha$ -hydroxyl acids to  $\alpha$ -keto acids is a rate-determining step, and better results are usually obtained using  $\alpha$ -keto acids under milder conditions. In addition to inorganic nitrogen resources (typically ammonia and NH<sub>2</sub>OH), some organic compounds containing amino groups have also been used to produce corresponding protected amino acids. Only a few studies focused on the chirality of amino acids. In recent years, some emerging technologies, such as photocatalysis and electrocatalysis, have been applied to the synthesis of amino acids.

The use of nitrogen-containing biomass resources can avoid the addition of nitrogen resources. The hydrolysis of protein produces a mixture of various amino acids. However, due to serious environmental concerns caused by strong acid/base, protein hydrolysis has not been widely employed for amino acids production. Abundant chitin is a promising substrate for amino acid synthesis because of the existing (protected) amino group. Amino

## 4 Conclusions and outlooks

### 4.1 Conclusions

With the increasing demand for amino acids, the green

sugar acids can be produced by the oxidation of chitin-derived amino sugars with satisfactory yields. Moreover, some amino alcohols derived from C–C cleavage of amino sugars have also been transformed into amino acids by simple oxidation reactions. Au and Ru catalysts showed good catalytic performance in some cases.

## 4.2 Outlooks

Although recent encouraging progress provides novel options for amino acid production except for fermentation, significantly more effort is needed to push the development in this area. Some possible research directions from our perspective are summarized as follows: (1) Novel chemical routes for the synthesis of amino acids must be developed, which will enrich the biorefinery roadmap. (2) Although both the precise analysis of side-products and deep insight of reaction mechanisms are significant for the design of catalytic systems, they are still lacking. Indeed, both experimental and theoretical calculations will be helpful. (3) Considering that the chirality has an evident effect on biological activity, the development of efficient approaches for the highly selective production of amino acids will be a challenging but important research direction. (4) The activity of some catalysts decreases drastically after catalytic reactions. In-depth understanding of the deactivation mechanism can guide the design of novel catalysts with higher stability. (5) Although some amino acids have been successfully obtained from biomass-based platform compounds, the use of more accessible biomass is highly desirable, despite numerous difficulties. With modern catalysis technologies, some integrated systems might be effective for the selective conversion of real biomass to fine chemicals like amino acids. (6) To develop efficient catalysts of non-precious metals to replace precious metals is consistently a promising research topic, which can reduce production costs and promote their industrial applications.

**Acknowledgments** The authors gratefully acknowledge the support of Natural Science Foundation of Chongqing (Grant Nos. cstc2020jcyj-msxmX0672, cstc2020jcyj-msxmX0839), the Science and Technology Research Program of Chongqing Municipal Education Commission (Grant No. KJQN202000826), Start-up Foundation of High-level Talents (Grant No. 1956037) in Chongqing Technology and Business University, and Key Disciplines of Chemical Engineering and Technology in Chongqing Colleges and Universities during the 13th Five Year Plan (Grant No. 950619013). The support from HKBU (RC-SGT2/19-20/SCI/009) is also appreciated.

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