Catalytic transformation of biomass-derived α-hydroxyl acids into amino acids[1]

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Abstract: The production of amino acids from renewable lignocellulosic biomass is attractive to help meet the world protein demand, but efficient and general chemical approaches are limited. Here, we report a heterogeneous catalyst that directly transforms lignocellulosic biomass-derived α-hydroxyl acids into α-amino acids, including alanine, leucine, aspartic acid, tyrosine, etc., in aqueous ammonia. Ruthenium nanoparticles supported on carbon nanotubes (Ru/CNT) exhibit exceptional efficiency compared to catalysts based on other metals, due to the ability of Ru to catalyze dehydrogenation reactions in the presence of NH3, which is the rate-determining step for amino acid formation. Alanine was obtained in 43% yield from glucose in a two-step chemical process, and therefore, the present strategy enables a new route for the transformation of lignocellulosic biomass into amino acids. Moreover, a conceptual process design employing membrane nanofiltration to facilitate product purification is proposed and validated by molecular simulations.

Keywords: amino acids; biomass; amination; ruthenium; glucose

1. Introduction (11-point boldface)

To date, sustainable and general approaches for the direct synthesis of amino acids from abundant and renewable feedstocks using NH_3 as nitrogen source are still very rare. In recent years, biomass-derived α-hydroxyl acids become readily accessible. Therefore, we envisaged that the direct amination of these acids with ammonia could offer a promising and general method for amino acids synthesis, with the replacement of the -OH group by an -NH2 group as the key chemical transformation. Herein, we report an efficient and stable heterogeneous catalytic system for the amination of lactic acid to afford alanine using ammonia as nitrogen source, which is applicable to the conversion of various α-hydroxyl acids into amino acids, providing an alternative route for value generation from biomass wastes.

2. Experimental

The catalytic transformation of lactic acid and other biomass-derived acids was performed in an autoclave. For example, for the conversion of lactic acid, the Ru/CNT catalyst and lactic acid were added to the reactor that had been pre-charged with aqueous ammonia. After the introduction of H2 at a pressure of 1 MPa, the reactor was placed in an electronic hotplate (typically 493 K). After a fixed time, the reaction was quickly terminated by cooling the reactor to room temperature in cold water. The catalytic transformation of glucose to lactic acid was performed in a round-bottom flask with Schlenk line. Degassed water was added to the reactor that had been pre-charged with glucose and Ba(OH)2 under N2 atmosphere. The flask was put in an oil batch on an electronic stirrer. After a fixed time, the liquid product was neutralized with sulfuric acid and filtered to remove Ba2+. The filtrate was added equal mole of NaOH to prevent organic acids lose during freeze-dry. After freezed-dry, the products were acidified with HCl and used as the substrates in the amination step. The liquid products were analyzed by high-performance liquid chromatography (HPLC, Shimazu LC-20A) equipped with both RI and UV detectors. Glucose and α-hydroxyl acids were quantified on an Agilent Hi-Plex H column (7.7 × 300 mm, 8 μm) using a dilute H2SO4 aqueous solution as the mobile phase, while amino acids were analyzed on a Poroshell 120 EC-C8 column (4.6 × 100 mm) by using a "pre-column derivatization method', where ortho-phthalaldehyde was used as the derivatization reagent. The dehydrogenation of isopropanol (IPA) over Ru and Pd catalysts were performed in a fixed bed flow reactor equipped with an online gas chromatography (GC, Agilent 7890A). A FID detector and an Agilent Cyclodex-B column (30 m x 250 μm x 0.25 μm) were used to detect and analyze IPA and gas products.

3. Results and discussion

We initially conducted the amination of lactic acid over several noble metal (i.e. Ru, Pd, Pt, Rh and Ir) nanoparticles loaded on CNT and Raney Ni in a batch reactor. The supported catalysts were prepared by impregnation of metal precursors with the CNT, followed by treatment in a H2/N2 (5%) atmosphere at 673 K to ensure complete reduction of the metals. X-ray diffraction (XRD) and transmission electron microscopy (TEM) confirm that all the metal nanoparticles are well dispersed on the CNT support and possess similar average sizes. Evaluation of the catalysts in lactic acid conversion in aqueous ammonia at 493 K for 2 hr, shows that the Ru/CNT are the most effective, providing alanine in 49% yield. Rh/CNT, Pt/CNT and Raney Ni afford alanine in yields of 18%, 12% and 8%, respectively, whereas Pd/CNT and Ir/CNT were essentially inactive. Since the Ru/CNT catalyst is exceptional for the amination of lactic acid, Ru nanoparticles were loaded on other supports including SiO_2, Al_2O_3, ZrO_2, CeO_2, and MgO, and evaluated under identical conditions. The alanine yields were distributed in a narrow range between 32% and 38%, irrespective of the nature of support material, i.e. whether it is acidic/basic, reducible/non-reducible, with the catalyst based on the CNT support remaining the most effective.

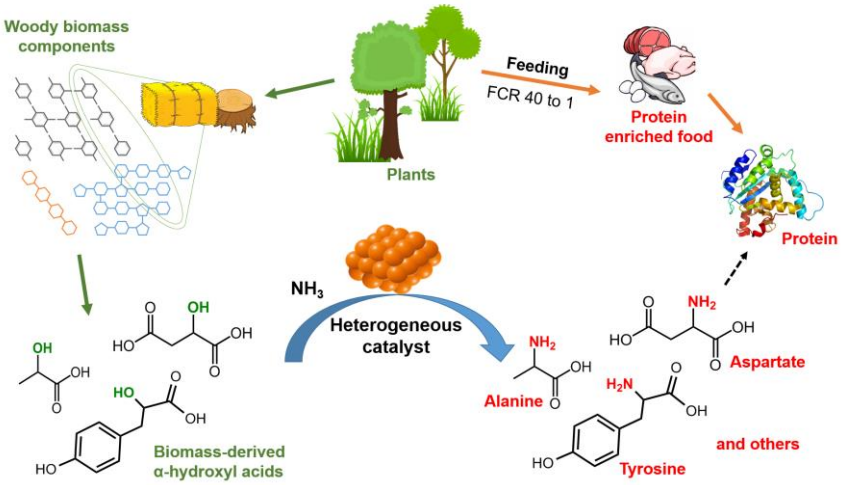
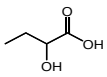
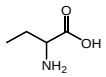
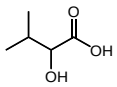
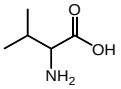
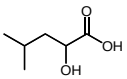
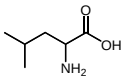
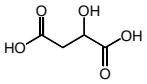
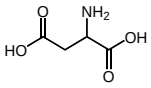
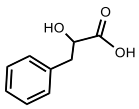
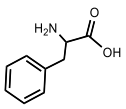
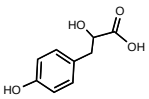
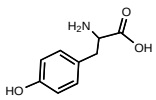


Figure 1. Catalytic transformation of biomass-derived α-hydroxyl acids into amino acids.

Apart from alanine, various other amino acids were prepared from biomass-derived α-hydroxyl acids in aqueous ammonia (Table 1). For example, α-aminobutyric acid, valine, and leucine were obtained from α-hydroxyl butyric acid, α-hydroxyl-3-methylbutyric acid, and α-hydroxyisocaproic acid, respectively (Table 1, entries 2, 4 and 6). By modification of the Ru/CNT catalyst with 10 wt % nickel or simply by adding a small amount of base (e.g. NaOH, KOH) to the reaction medium, the formation of amino acids was markedly enhanced (Table 1, entries 3, 5 and 7). The yields of α-amino butyric acid, valine, and leucine reached 73%, 60%, and 69%, respectively, in the modified catalytic systems. The synthesis of aspartic acid was also achieved by amination of 2-hydroxysuccinic acid. The yield of 27% is lower than the other substrates tested, possibly due to the steric hindrance of the terminal acid group (Table 1, entry 8). In addition to aliphatic acids, the production of aromatic amino acids was demonstrated from lignin-derived carboxylic acids (Table 1, entries 9 and 10). For instance, an impressive tyrosine yield of 80% was obtained using the Ni-modified Ru/CNT catalyst.

Table 1. Catalytic transformation of different biomass-derived hydroxyl acids to corresponding amino acids using Ru/CNT catalysts

Entry	Substrate	Product	Yield [%]
1[b]		 Alanine	62
2		 α-Aminobutyric acid	66
3[b]			73
4		 Valine	48
5[b]			60
6		 Leucine	49
7[c]			69
8[c]		 Aspartic acid	27
9[b]		 Phenylalanine	30
10[b]		 Tyrosine	80

[a]Reaction conditions: 0.5 mmol substrate, 0.05 g Ru/CNT (Ru loading 3 wt %), 2.5 mL aqueous NH_3 (25 wt %), 1 MPa H_2, 493 K, 2 hr.
[b]Ru/CNT was modified with 10 wt % Ni.
[c]KOH or NaOH (1 mmol) was added in the solution.

4. Conclusions

To summarize, we have developed an efficient, stable heterogeneous catalytic system for the synthesis of a variety of amino acids from biomass-derived carboxylic acids, in which dehydrogenation of the hydroxyl group is the rate-determining step. Compared to other noble metal catalysts, Ru exhibits considerably enhanced dehydrogenation activity in the presence of NH3, resulting in a unique performance for the reaction. The direct conversion of glucose into alanine is achieved following a simple, two-step chemical protocol. Nanofiltration appears to be an effective way to separate the product, and ZIF-25 has been identified as a promising membrane material to purify alanine from the reaction mixture. Our work demonstrates the feasibility of chemical transformation of woody biomass components into amino acids, and opens the way to the production of high-value proteins from agricultural wastes via chemical routes in the future.

References

1. The research article associated with this conference abstract has been submitted and is currently under review.