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Highlight

Chemical transformation of sugars into amino acids

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Amino acids are essential to life. As everyone learns at school, in the Miller's famous experiment a mixture of methane, ammonia, hydrogen and water under continuous electrical sparks was converted into a variety of amino acids, including glycine, alanine, aspartic acid, and α-aminobutyric acid as initially identified [1], and many more in a much more recent study [2]. This chemical process establishes the foundation of modern understanding on how life occurs on earth. Nowadays, amino acids find wide applications in industry, but they are primarily manufactured via microbial cultivation processes suffering a number of limitations. Sustainable and generalizable chemical approaches for the direct synthesis of amino acids from abundant and renewable carbon feedstocks using NH_3 are vastly unknown.

A new chemical route to make a series of amino acids from woody biomass derivatives has been very recently developed, led by Prof. Ning Yan's group at National University of Singapore, under collaboration with Prof. Ye Wang's group at Xiamen University and a few other groups [3]. Their new system can be regarded as a modified Miller's system, where methane is replaced by a purposely selected organic acid precursor derived from woody biomass, while the electrical spark is replaced by a supported Ru catalyst (Fig. 1). Empowered by the combined use of proper starting materials and an efficient catalyst, one amino acid is obtained at a time, and the system is effective in producing at least 6 amino acids.

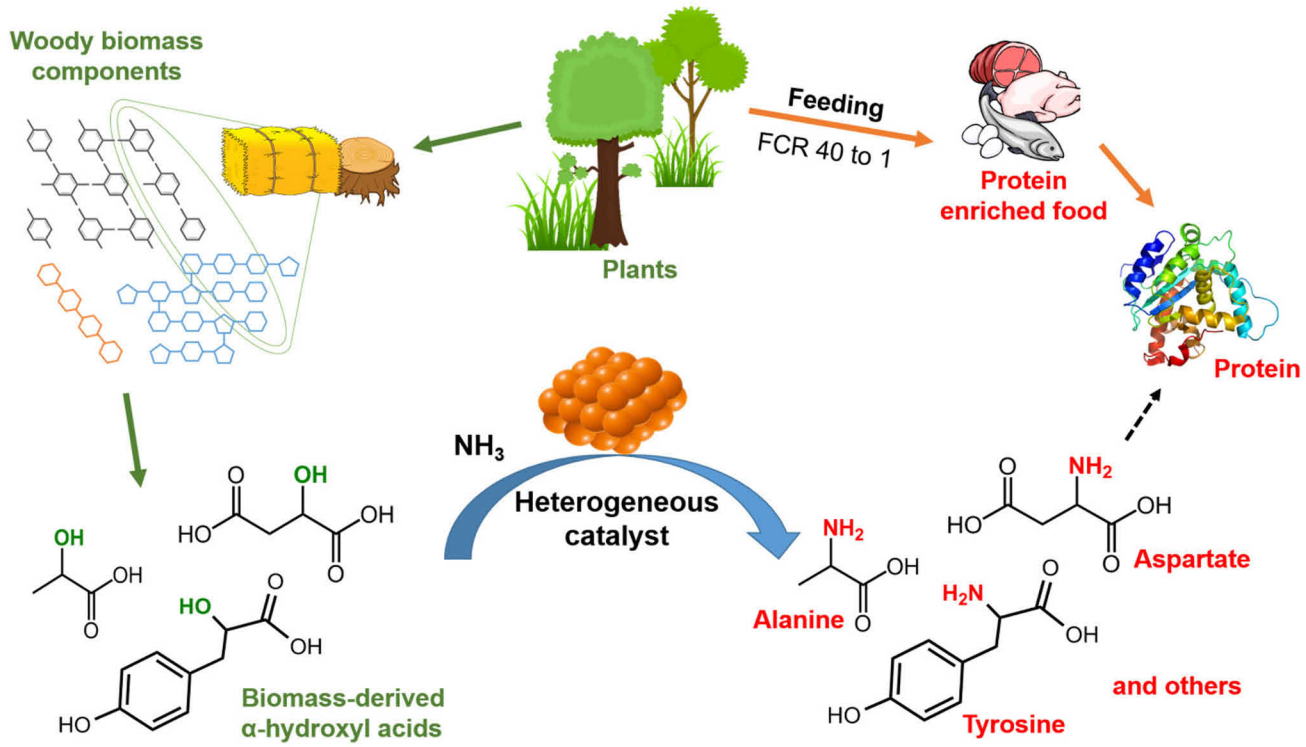

Fig. 1. Catalytic transformation of biomass-derived α-hydroxyl acids into amino acids (FCR refers to feed conversion ratio, figure taken from Ref. [3]).

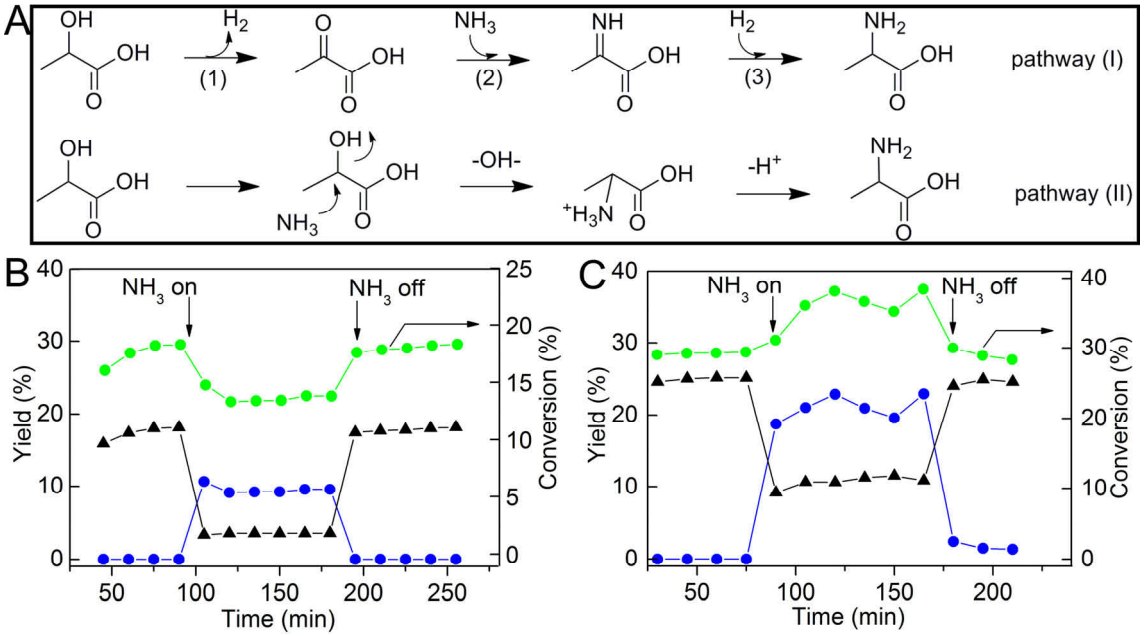

Fig. 2. (A) Two possible reaction pathways for amination of lactic acid to alanine. (B) Dehydrogenation of isopropanol catalyzed by Pd/CNT and (C) Ru/CNT under a H_2 atmosphere in a fixed-bed flow reactor, (●) isopropanol conversion, (▲) acetone yield, (●) isopropylamine yield. Reaction conditions: 0.050 g catalyst, 2 μL/min isopropanol, 50 mL/min total flow rate, 473 K, 1 atm, 8 mL/min NH_3 flow rate (figure taken from Ref. [3]).

There are two key functional groups in an amino acid, i.e., amine (-NH_2) and carboxyl acid (-COOH) groups. The strategy utilizes a two-step protocol to construct carboxyl group and amine group, respectively, from woody biomass components. Sugars or other types of biomass are firstly degraded into certain α-hydroxyl acids—a step that has been discovered and extensively studied in the past decade [4]. In a second step, the hydroxyl group is transformed into the amine group, using ammonia as the nitrogen source. The latter is an amination reaction of biomass derived alcohols, in line with the team's long term effort in making renewable nitrogen-containing chemicals and materials [5–7]. Previously, Dalian Institute of Chemical Physics has reported a two-step protocol to convert cellulose into ethanol amine via glycolaldehyde as an intermediate [8]. The strategy herein takes that idea one step further.

In this study, the researchers used transformation of lactic acid to alanine in aqueous ammonia as a probe reaction, and screened a number of metal catalysts at 493 K for 2 h. Ru/CNT, prepared by impregnation method and reduced under H_2, afforded higher activity than other noble metal catalysts (Pd/CNT, Pt/CNT, Rh/CNT, and Ir/CNT) and Raney Ni. The reaction follows a dehydrogenation-reductive amination pathway [9], where pyruvic acid was the key intermediate and dehydrogenation was the rate-determining step (Fig. 2A). Metallic Ru NPs were confirmed as the catalytically active species via several techniques including XANES, EXAFS, XPS, and H_2-TPR. In the presence of NH_3, interestingly, the dehydrogenation ability of Ru nanoparticles (NPs) was significantly enhanced, while that for other metal NPs were suppressed, endowing Ru superior activity in amino acid formation (Fig. 2B and Fig. 2C).

The Ru/CNT catalyst was tested in a recycling experiment of 9 consecutive runs, achieving a total turnover number of 575 per surface Ru atom. Under optimized reaction conditions, the Ru/CNT catalyst was further modified by doping Ni as the second metal where the yield of alanine from lactic acid was improved to 62%. Based on this result, glucose was converted to

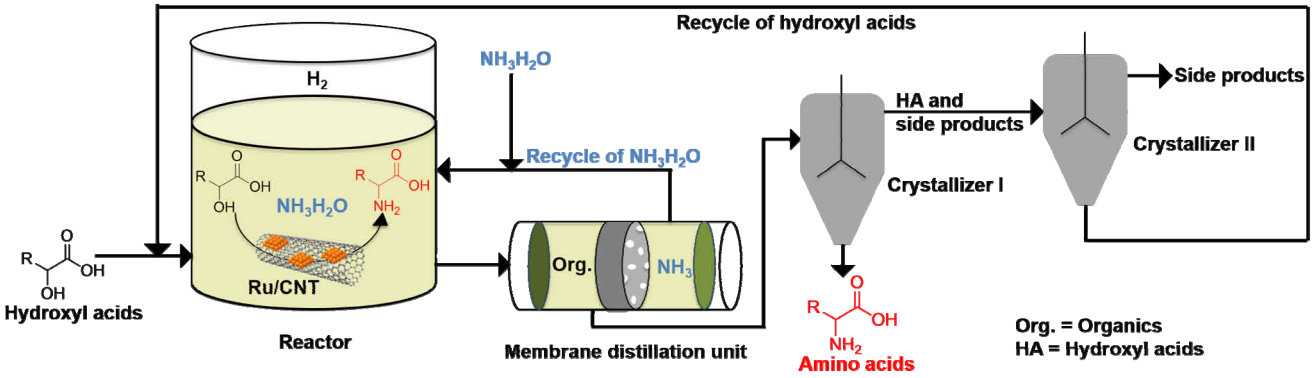

Fig. 3. A conceptual process diagram consists of a reactor, a membrane distillation unit, and two crystallizers (figure taken from Ref. [3]).