ISGC 2019
May 13rd - 17th

N°245 / OC
TOPIC(s) : Biomass conversion / Homogenous, heterogenous and biocatalysis

Rh-catalysed hydrogenation of amino acids to bio-based amino alcohols: tackling challenging substrates and application to protein hydrolysates

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PURPOSE OF THE ABSTRACT

The synthesis of bulk and fine chemicals from renewable resources is an important challenge according to the principles of green chemistry. Today, huge amounts of protein-rich waste streams are available from agro-industry and bio-fuel production. The protein fraction generally accounts for 20-40 wt% of the dry biomass and is readily hydrolyzed to (a mix of) amino acids.[1] Whereas animal feed formulation is nowadays the major route for valorization, the nitrogen efficiency is rather low. Therefore, these streams are an excellent resource for producing N-containing chemicals.

We focus on amino alcohols, because the atom economy of both carbon and nitrogen is excellent. Amino alcohols have applications as building blocks and chiral auxiliaries in the synthesis of pharmaceuticals and agrochemicals. In the past, procedures for amino acid reduction relied on stoichiometric amounts of metal hydrides, such as $LiAlH_4$ or $NaBH_4$.[2] On the other hand, Ru- and Rh-catalyzed hydrogenation produces only water as a by-product. Nevertheless, the scope is hitherto limited to amino acids with an aliphatic side chain, serine and lysine.[3,4,5] In this work, the substrate scope of the Rh-catalyzed hydrogenation is extended towards a broad scope of (challenging) amino acids and a protein hydrolysate.

Using a Rh-MoOx/SiO_2 catalyst, all natural amino acids are converted towards the corresponding amino alcohols with good conversion and selectivity. The bimetallic nature of this catalyst enables COOH hydrogenation by facilitating the adsorption of the amino acid by hydrogen bond interactions between COOH and MoOx species.[6]

Special attention is devoted to the hydrogenation of glutamic acid (Glu), which contains an additional, though less reactive carboxylic acid in the side chain and. Furthermore, Glu is the most abundant amino acid in plant protein hydrolysates. Glutamidiol is obtained in good yield (77%) at full conversion. Side products originate from hydrogenolysis and cyclization, but are useful as well (Figure 1). [7]

Even S-containing amino acids, cysteine (Cys) and methionine (Met), are addressed. It is well known in the literature that platinum group metals (Pt, Pd, Ru, Rh, ?) are sensitive to sulfur containing compounds:[8,9] due to irreversible coordination of the thiol (from Cys) or thioether (from Met) on the metal surface, the catalyst is deactivated. However, by performing a simple oxidation prior to the hydrogenation, catalyst poisoning is avoided. The resulting sulfonic acid and sulfone functionalities, respectively from Cys and Met, do not hinder catalytic activity and the corresponding amino alcohols are obtained with high conversion and selectivity.[7]

Since protein waste streams consist of entire proteins and peptides instead of individual amino acids and separation of amino acids is hard to accomplish, a model protein for animal protein waste fractions (bovine serum albumin (BSA)), is used as a starting material for hydrogenation. Oxidation and subsequent hydrolysis of BSA generates a mixture of all natural amino acids and cysteic acid and methionine sulfone, the oxidized products of cysteine and methionine respectively. An overall conversion and selectivity to amino alcohols of 90% and 88%

respectively, are obtained for almost all amino acids after 48 h of hydrogenation.[7] In this way, a protein hydrolysate is successfully hydrogenated to the corresponding amino alcohols without the need for an additional, expensive and difficult separation step, which clearly provides opportunities for the valorization of protein-rich waste streams.

FIGURES

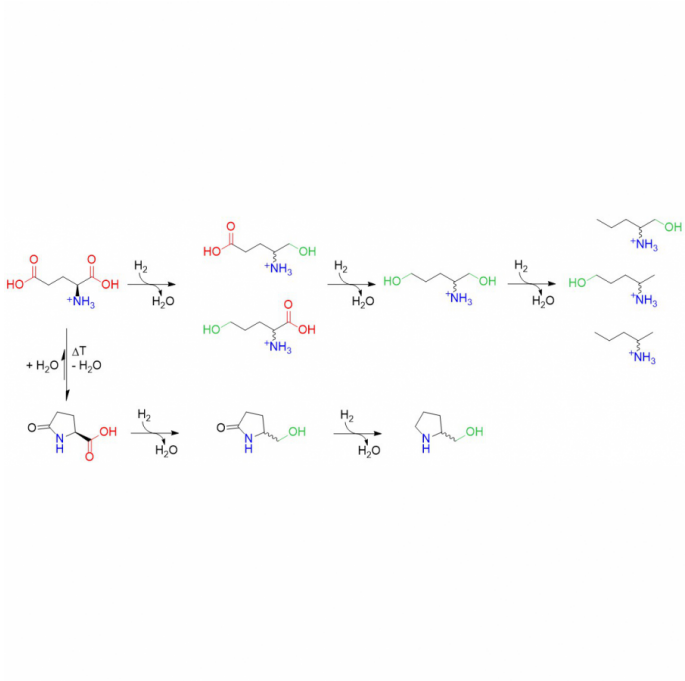

FIGURE 1

Rhodium-catalyzed hydrogenation of glutamic acid

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FIGURE 2

KEYWORDS

Hydrogenation | Amino acids | Amino alcohols | Rhodium

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