Hydrogenation of the full scope of natural amino acids and a protein hydrolysate into amino alcohols

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Abstract: Valorisation of renewable resources, e.g. protein-rich waste, for the production of chemicals is a major challenge. These protein fractions are mainly used as feed resulting in low N-efficiency. A more interesting route is hydrogenating amino acids into amino alcohols, providing very high C and N atom economies. Here, for the first time, the full scope of amino acids is successfully hydrogenated with a Rh-MoO_x/SiO_2 catalyst. The S-containing amino acids are addressed since cysteine and methionine poison the catalyst. However, oxidation prior to hydrogenation, avoids poisoning. In this way, even a protein hydrolysate is successfully hydrogenated to the corresponding amino alcohols.
Keywords: Bio-based amino alcohols; Hydrogenation; Heterogeneous catalysis.

1. Introduction

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 hydrolysed to (a mix of) amino acids.[1] Whereas animal feed formulation is nowadays the major route for valorisation, 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 or can be used as polymer precursors, e.g. epoxy thermosets. 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-catalysed 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-catalysed hydrogenation is extended towards the full spectrum of natural amino acids and hydrogenation is successfully applied to a protein hydrolysate.

2. Experimental (or Theoretical)

Rh-MoO_x/SiO_2 is prepared via a consecutive impregnation procedure with a Rh precursor solution and a Mo precursor solution respectively. Afterwards, the precatalyst is calcined and reduced. Hydrogenation reactions are performed in a Teflon lined 50 mL high-pressure stainless-steel Parr reactor at a pressure of 70 bar H_2, temperature of 80 °C and acid concentration of 0.3 M H_3PO_4.

3. Results and discussion

Using a Rh-MoO_x/SiO_2 catalyst, the full scope of natural amino acids is converted towards the corresponding amino alcohols with good conversion and selectivity. The bimetallic nature of this catalyst facilitates -COOH hydrogenation by facilitating the adsorption of the amino acid by hydrogen bond interactions between -COOH and MoO_x 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. Glutamidiol is obtained with high selectivity at full conversion. Side products originate from hydrogenolysis and cyclization, but are useful as well (Figure 1).

Since Glu is the most abundant amino acid in plant protein hydrolysates, catalytic hydrogenation of amino acids provides opportunities for protein waste valorisation.

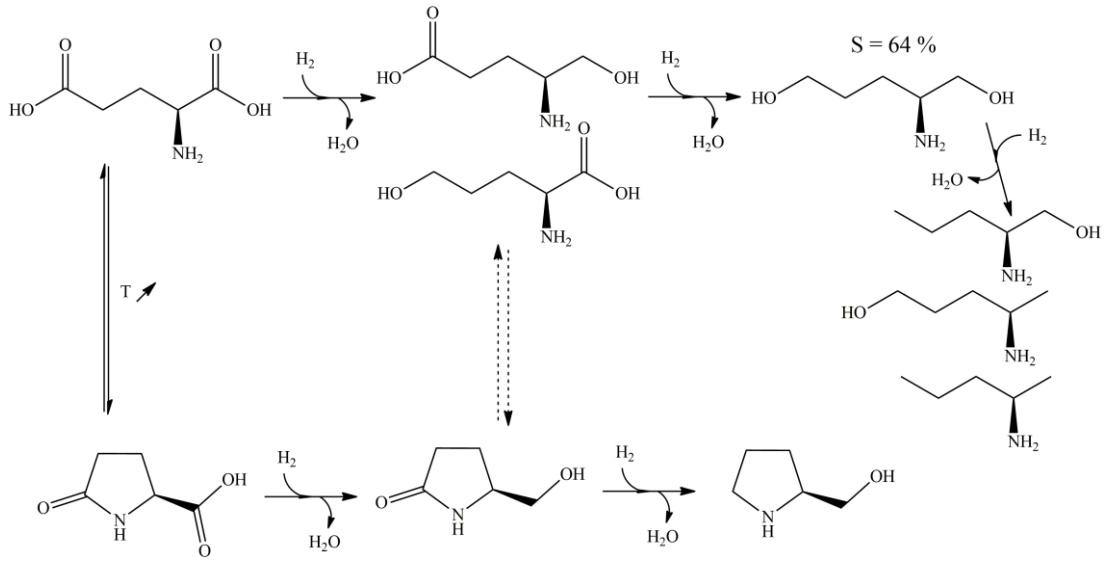

Figure 1. Rhodium-catalyzed hydrogenation of glutamic acid.

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 sulphur containing compounds:[7,8] 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 produced.

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. Good to excellent conversions (≥ 87%) and selectivities (≥ 76%) are obtained for almost all amino acids after 48 h of hydrogenation.

4. Conclusions

For the first time, the full scope of amino acids can be hydrogenated to amino alcohols in good conversion and selectivity using a bimetallic Rh-MoO_x/SiO_2 catalyst. Even glutamic acid, with an additional, less reactive -COOH functional group in the side chain, and S-containing amino acids are successfully hydrogenated. Moreover, 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 valorisation of protein-rich waste streams. Furthermore, the atom economy of both carbon and nitrogen is excellent, and only water is produced as a by-product, which are major assets in sustainable, green chemistry.

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