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RUTHENIUM-CATALYZED AEROBIC OXIDATIVE DECARBOXYLATION OF AMINO ACIDS: A GREEN, ZERO-WASTE ROUTE FOR BIO-BASED NITRILES PRODUCTION

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ABSTRACT

Nitrogen-based functionalities, in particular amines and amides, are present in a broad range of commodity and fine chemicals. They are often obtained by hydrogenation or hydration of nitriles, which are themselves the result of reactions such as olefin ammoxidation or cyanide addition. Exemplary large-scale processes are the ammoxidation of propylene into acrylonitrile or the hydrocyanation of butadiene into adiponitrile. However, the necessity of toxic reagents (e.g. HCN) or the harsh process conditions are strong incentives to explore alternative milder production routes.

Nitrogen-containing biomass constituents, in particular the protein fraction, provide an excellent renewable feedstock for such purpose. Protein-rich waste streams are abundantly available from agro-industry and biofuel production and can contain up to 20-40 wt% of proteins.[1] Recently, it has been shown that the amino acids, obtained via hydrolytic protein depolymerization, can be transformed smoothly and selectively into - often functionalized - nitriles via oxidative decarboxylation mediated by hypobromite species.[2] Instead of using halogenated organic reagents[3] or hypohalite oxidants,[4] catalytic amounts of a bromide salt are oxidized in situ using H₂O₂ and a heterogeneous catalyst.

Here, we present a more benign strategy for oxidative decarboxylation of amino acids into nitriles, which allows using dioxygen as terminal oxidant. Heterogeneous catalysts, based on ionic ruthenium species immobilized on a solid support, e.g. Ru(OH)_x/Al₂O₃, have been reported to facilitate aerobic oxidation of primary and secondary amines.[5] This was proven to be a powerful system for imine or nitrile synthesis, but now their remarkable activity in amino acid oxidation has been uncovered. The reaction is run in water with high conversion and good nitrile selectivity. The most important byproduct, viz. the amide, is due to ruthenium-catalyzed nitrile hydrolysis,[6] which is unavoidable under these conditions. This was illustrated for amino acids with an aliphatic side chain, such as alanine, valine, leucine and isoleucine, as well as for compounds with a functionalized side chain, such as glutamic acid (Scheme 1). The latter one is the most abundant amino acid constituent in plant biomass and the derived nitrile product is a precursor for acrylonitrile[4] and succinonitrile.[7] In conclusion, this strikingly green oxidative transformation allows producing bio-based nitriles in the absence of any halide source. In this way, the N-cycle can be closed by converting waste compounds into useful chemicals.

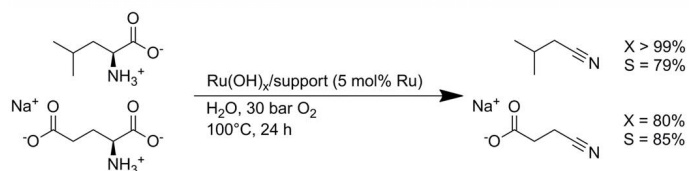


FIG1 LEGEND

Scheme 1. Ruthenium-catalyzed aerobic oxidative decarboxylation of leucine and glutamic acid.

FIG2 LEGEND

KEYWORDS

amino acids | biomass | decarboxylation | heterogeneous catalysis | oxygen | nitriles | ruthenium

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