

Reductive amination of 5-formyl-2-furancarboxylic acid to 5-(aminomethyl)furan-2-carboxylic acid

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1. INTRODUCTION

5-(Aminomethyl)furan-2-carboxylic acid (AMFCA) is a potential monomer for the production of biobased aromatic or semi-aromatic polyamides. Biomass-derived 5-formyl-2-furan carboxylic acid (FFCA) can be converted to AMFCA via reductive amination as shown in Fig. 1, but no promising strategy has been developed so far. In this study we have studied reductive amination of FFCA using stable and highly active heterogeneous catalyst.

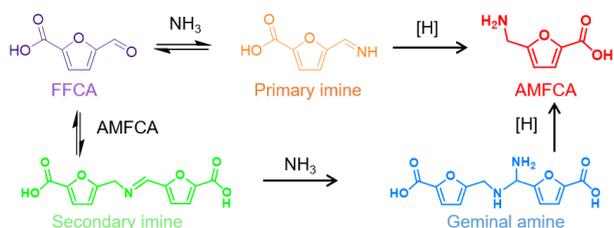


Fig. 1 Reaction pathways for the conversion of FFCA to AMFCA by reductive amination through primary imine and secondary imine.

Recently, cobalt phosphide nanorod (Co₂P) catalyst containing coordinatively unsaturated Co–Co active sites was reported as a new class of air-stable, highly active, and reusable heterogeneous catalysts for the reductive amination of carbonyl compounds to their corresponding primary amines using NH₃ or NH₄OAc as green amination reagents.^{1,2} The air stability and high activity of the Co₂P is noteworthy, as conventional Co catalysts are air-sensitive (pyrophoric) and show very limited activity for this transformation under mild reaction conditions.^{1,2} We have applied the Co₂P catalyst to reductive amination of FFCA to AMFCA.

2. EXPERIMENTAL

Co₂P was prepared according to literature.² Catalytic reactions were performed in Teflon lined batch reactors. Reactors were loaded with 0.5 mmol of FFCA, 5 mmol NH₄OAc, 0.03 mmol Co₂P, 2 mL MeOH, and 1 mL H₂O, then pressurized with 0.5 MPa H₂ and heated to 120°C for a pre-set duration. Reaction mixtures were analyzed by HPLC using an Shodex ODP2 HP-4E column and mobile phase using phosphate buffer (pH10) 23% and MeCN 77%.

3. RESULTS AND DISCUSSION

Reductive amination of FFCA in water in the presence of NH₃ or NH₄OAc produces undetectable byproducts always in 30-50% selectivity. However, such byproducts formation was found to be suppressed largely in a methanol-water (2:1 v/v) mixture using NH₄OAc as shown in Fig. 2. In this reaction system, FFCA was present in the mixture of bare form and dimethylacetal form (FFCA-acetal). FFCA and FFCA-acetal decreased with time and finally disappeared (~0%) at 180 min. The product found after 30 min was the secondary imine formed from FFCA and AMFCA (Fig 1). Free AMFCA was detected after 60 minutes, together with a decline in secondary imine. Maximum AMFCA yield was 95% at full conversion, together with minor byproducts including as 5-(hydroxymethyl)-2-furan carboxylic acid (HMFCFA) in only 5%. AMFCA formed at the initial stage via primary imine is consumed for the formation of secondary imine, as shown in Figure 1. Low yield of secondary imine and steep increase in AMFCA yield after secondary imine formation suggested that primary imine pathway is slow compared to secondary imine pathway. Increase in AMFCA concentration promoted secondary imine, which leads to more efficient production of AMFCA.

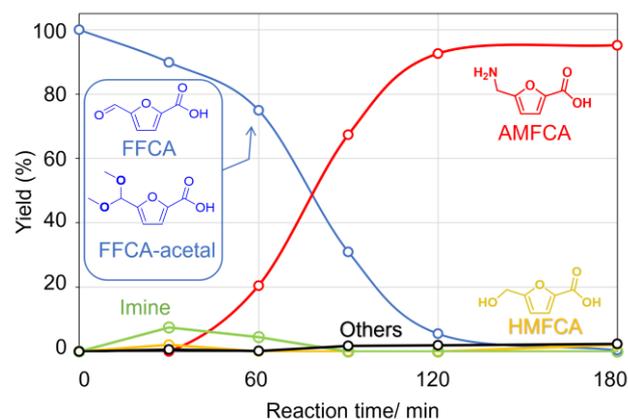


Fig. 2 Time course for reductive amination of FFCA in methanol-water mixture using NH₄OAc; AMFCA yield (red), FFCA and FFCA-acetal yield (blue), imine yield (green), and others (black).

(1) Mitsudome, T. *et al.*, *Chem. Sci.* **2020**, *11* (26), 6682–6689.

(2) Sheng, M. *et al.*, *JACS Au* **2021**, *1* (4), 501–507.