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Single-Reactor Tandem Oxidation-Amination Process for the Synthesis of Furan Diamines from 5-Hydroxymethylfurfural

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PURPOSE OF THE ABSTRACT

5-Hydroxymethylfurfural (HMF), derived from carbohydrates, is an attractive platform molecule with huge market potential.1 Amines can be accessed from HMF by reductive amination over catalysts operating under the H2 borrowing mechanism. However, the catalytic activity is conditioned by the divergent reactivity of the ?CH=O and ?OH groups in HMF. Indeed, the ?OH group is poorly reactive and examples of catalysts affording direct transformation of HMF into diamines are scarce (Figure 1A).2 To access diamines, an alternative yet simple strategy encompasses the oxidation of HMF to DFF, followed by reductive amination of DFF to the diamine, in a two-reactor process (Figure 1B).

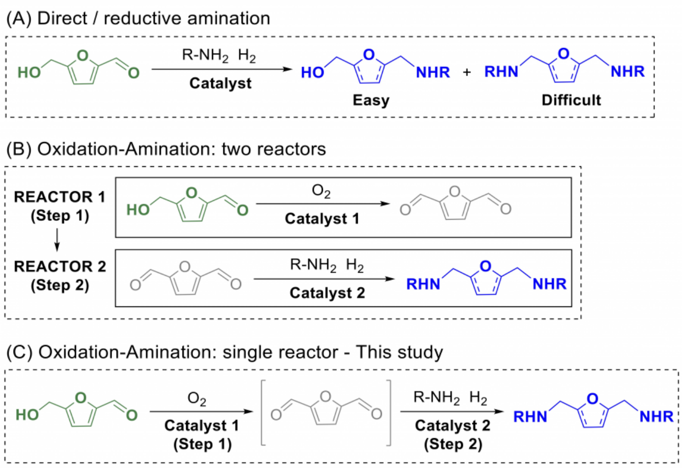
Herein we report a single-reactor tandem oxidation-amination process for preparing secondary furan diamines from HMF comprising two in situ consecutive steps (Figure 1C): (1) aerobic oxidation of HMF to DFF, and (2) reductive amination of DFF to diamines. Compared to a two-reactor process, such a process affords a higher degree of intensification and avoids separation of the DFF intermediate. A key challenge is to engineer a bifunctional catalyst with high activity and selectivity for both steps, which is the goal of this study.

First, we tested a series of catalysts for the aerobic oxidation of HMF to DFF. The reaction conditions were set at 110 °C for 6 h, 3 bar O2 and a HMF/metal molar ratio of 47 in 1,4-dioxane. Among the catalysts, 5%Ru/C displays 98% DFF selectivity with 91% HMF conversion. Next, we studied the performance of a family of catalysts for the reductive amination of DFF with BuNH2 and H2. Given the results for HMF oxidation, 1,4-dioxane was used as solvent, with high solubility of amination products. Upon contact of DFF with BuNH2, fast condensation to furfuryldiimine (1a) occurs. The hydrogenation of 1a can yield three potential amination products, i.e. the furan diamine 2a and THF-diamines 3a and 4a, depending on the catalyst used. In particular, 5%Pd/C favors 2a and 4a with 81% and 10% selectivity, respectively, and 93% carbon balance at optimized conditions. Noteworthy, the intermediate 3a is not observed, as well as difurfuryl and THF-diols.

Given these results, we studied the oxidation and reductive amination steps over a mixture of 5%Ru/C + 5%Pd/C. At an optimal Ru/Pd molar ratio of 2.8, both steps proceed with high activity and selectivity with a maximum 2a yield of 97% and 75% for the second step at 50 °C and 90 °C, respectively, and 20 bar H2 after 1 h. We then investigated the single-reactor tandem oxidation-amination reaction of HMF with BuNH2. HMF (0.5 mmol) was charged to the reactor with 1,4-dioxane (2 mL) and 5%Ru/C + 5%Pd/C (Ru/Pd = 2.8 mol/mol), and the reaction was carried out at 90 °C and 20 bar O2 for 16 h. After this time, the O2 pressure was released, BuNH2 (0.15 mL) was added to the reactor with 20 bar H2, and the reaction was conducted at 50 °C for 1 h (Figure 2). The 2a and 4a yield is 75% and 9%, respectively. H2-TPR characterization of the fresh and spent 5%Ru/C + 5%Ru/C mixture reveals that only a few amount of Pd/C is oxidized during the oxidation step, and that it can be fast reduced during the reductive amination step, making it active for the reaction.

With these results, bifunctional Ru-Pd catalysts were prepared by the IWI and precipitation-reduction methods with a Ru/Pd molar ratio of 2.8, and were tested for the single-reactor tandem oxidation-amination reaction. Among the catalysts, Pd(Ru/C)_IWI reduced under H2 displayed the best performance with 2a yield of 67%. A recyclability test was carried out for Pd(Ru/C)_IWI. The catalyst showed comparable activity and slightly higher stability than the combined 5%Ru/C + 5%Pd/C system.

FIGURES



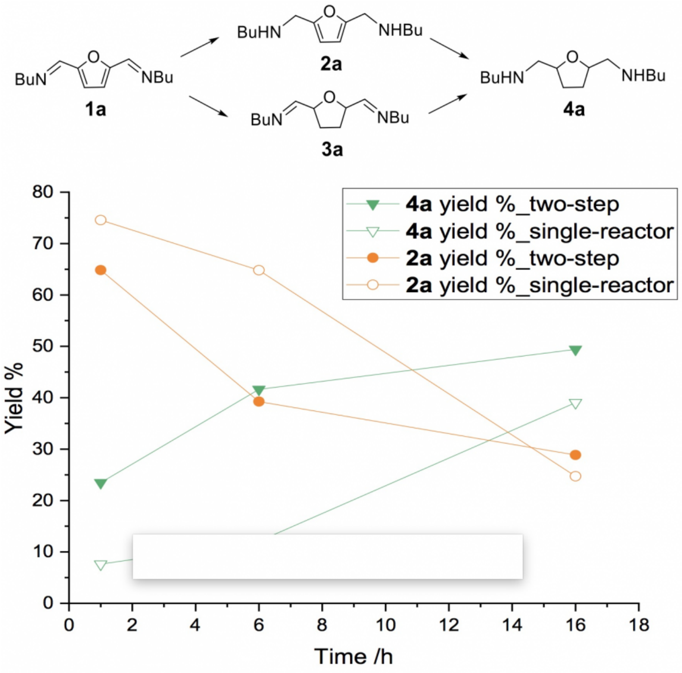


FIGURE 1

Figure 1.

Strategies for preparing secondary furan diamines from HMF: (A) direct/reductive amination; (B) oxidation-amination in two reactors; and (C) oxidation-amination in single reactor.

FIGURE 2

Figure 2

Amination of 1-octanol with NH3; A) Effect of Ni loading, B) Recycling study. Reaction conditions: 1-octanol-1.3 mmol, T- 160 oC, NH3- 7 bar, Time- 4 h, rpm- 600, Solvent- 3mL o-xylene, Cat.-55 mg.

KEYWORDS

Single-reactor | HMF | Oxidation-Amination | Diamines

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