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Glycolaldehyde as Bio-based C2 Platform Chemical: Catalytic Reductive Amination of vicinal Hydroxyl Aldehydes

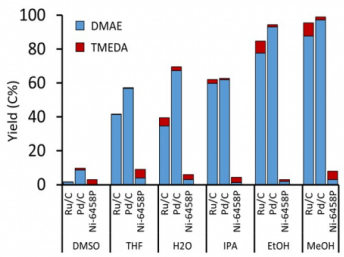
AUTHORS

Sofie VAN PRAET / KU LEUVEN, CELESTIJNENLAAN 200F, LEUVEN
Benjamin VERMEEREN / KU LEUVEN, CELESTIJNENLAAN 200F, LEUVEN

PURPOSE OF THE ABSTRACT

The market demand for alkanolamines (AA) and ethylene diamines (DA) has rapidly increased in recent years due to their use in coatings, polyurethane synthesis, and their more sustainably driven applications such as water treatment and acid gas scavenging (including CO2 and H2S). However, the current production of AAs and DAs can still ameliorate in terms of green chemistry and sustainability since it involves the reaction of oxiranes (mainly ethylene oxide) or chlorinated hydrocarbons (mostly ethylene) with ammonia, primary or secondary amines. Recently, in collaboration with industry, our research group published a review that critically discusses the substitution of ethylene oxide by bio-based structural analogs. Glycolaldehyde (GA) was proposed as a substitute for the current EO-based platform molecules. Although the unique asymmetric difunctionality of GA contributes to its remarkable reactivity, this research elaborates on the obstacles associated with this reactivity. For instance, ?-hydroxycarbonyl groups can easily be reduced catalytically to alcohols. They are susceptible to aldol condensations and react readily with amines, to form an even more labile imine intermediate prone to Maillard reactions, caramelization reactions, Amadori rearrangements, and, particularly for C2 ?-hydroxycarbonyl, keto-enol tautomerization. The challenge of the reductive amination of GA is balancing the different thermodynamic and kinetic parameters that control the reaction selectivity. Here, we report the first systematic study of solvent, reaction conditions, and catalyst for the reductive amination of GA with ammonia and commercial methylamines to achieve high AA and DA product yields.

FIGURES



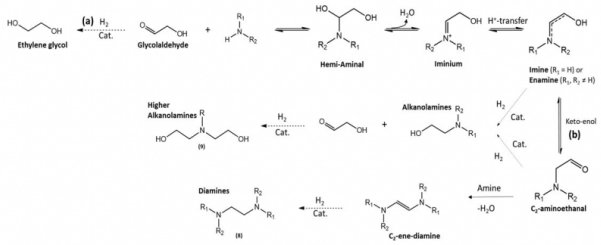


FIGURE 1

The influence of catalyst and sovlent on the product selectivity

The effect of solvent and catalyst on the reductive amination of GA with DMA forming AA (DMAE) and DA (TMEDA).

FIGURE 2

reaction mechanism for the reductive amination of GA.

no legend

KEYWORDS

Biomass | heterogeneous catalysis | Glycolaldehyde | sustainablilty

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