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Cu-catalyzed sustainable synthesis of formamide with glycerol derivatives as carbonyl sources via a radical-relay mechanism

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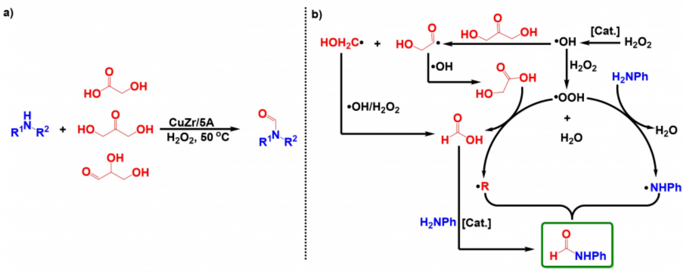
PURPOSE OF THE ABSTRACT

Formamide is widely used as important precursors or intermediates in synthetic and medicinal chemistry, but its industry production requires using highly toxic CO, resulting in serious safety hazard.[1] The utilization of bio-based platform molecules derived from glycerol such as glycolic acid (GA), 1,3-dihydroxyacetone (DHA) and glycerolaldehyde (GLA)[2] can promote the valorization of glycerol at some extent and turns waste into treasure. Therefore, it will be ideal if bio-based glycerol can be directly used as carbonyl sources for formamide synthesis. Based on our continuous efforts in synthesis of nitrogen-containing chemicals from renewable feedstocks,[3-5] bimetallic catalysts CuM/5A (M= Ni, Zr, Mo, Ag, Pd, Rh) prepared by the ion-exchange method were applied for N-formylation of amines to formamide with glycerol derivatives as carbonyl sources and H2O2 as oxidants (Scheme 1a).

Activity test results showed that CuZr/5A catalyst exhibited the best catalytic performance (Figure 1a). NH3-TPD results indicated that introducing the second metal leads to the reduction of acid sites, especially the medium-strong acid sites and the most active CuZr/5A catalyst has the least amount of medium-strong acid sites (Figure 1b), suggesting that the presence of medium-strong acid sites might be adverse to the product formation. Comparison of H2O2 activated by different catalysts showed that all the catalysts can activate H2O2 to generate ?OH and ?OOH radicals but CuZr/5A catalyst has the highest proportion of ?OOH radicals, implying that Zr can promote the formation of ?OOH radicals (Figure 1c).

EPR spin trapping experiments with DMPO revealed the formation of radical intermediates such as ?CH2OH, ?C(=O)CH2OH, ?R (organic carbon-centered radicals) and ?NHPh (Figure 1d and 1e), where the first two stem from the attack of ?OH to DHA and the last two from the attack of ?OOH to GA intermediate and aniline respectively. Operando ATR-FTIR detected the formation of GA and FA intermediates at 1728 and 1710 cm-1 respectively (Figure 1f). Control experiments implied that Zr can greatly boost the C-C bond cleavage in GA and that all the carbon atoms in glycerol derivatives can be transferred into formamide products. Based on all these results, a possible reaction mechanism was proposed (Scheme 1b). The concept of glycerol derivatives directly as carbonyl sources via oxidative C-C bond cleavage can be extended in the valorization of other biomass-based platform molecules.

FIGURES



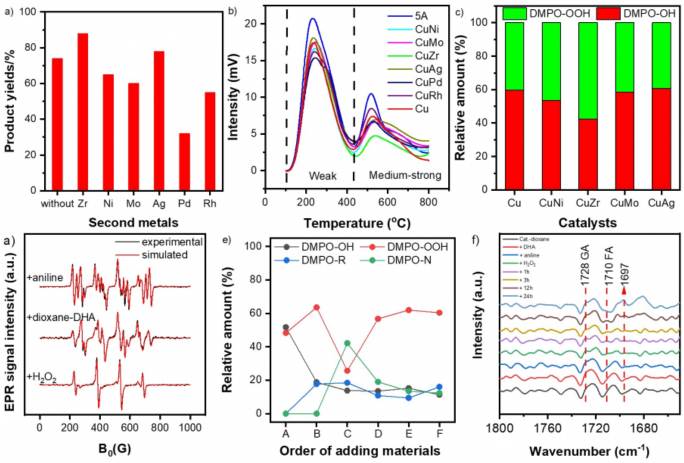


FIGURE 1

Scheme 1

a) Synthesis of formamides with glycerol derivatives as the carbonyl source, b) Proposed reaction mechanism.

FIGURE 2

Figure 1

a) Activity test, b) NH3-TPD, c) H2O2 activation, d) EPR spectra and e) proportion of DMPO spin adducts (A: CuZr/5A-H2O2, B: +DHA-1,4-dioxane, C: +aniline, D: +1 h, E: +4 h, F: +7 h), f) 2nd derivative of operando ATR-FTIR spectra.

KEYWORDS

glycerol derivatives | biomass conversion | N-formylation | formamide

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