Sustainable Co-Synthesis of Glycolic Acid, Formamides, and Formates from 1,3-Dihydroxyacetone by a Cu/Al₂O₃ Catalyst with a Single Active Sites


Co-Synthesis of Glycolic Acids, Formamides, and Formates on Copper/Alumina

**Significance:** An alumina-supported copper catalyst (Cu/Al₂O₃) was prepared by mixing copper(II) chloride with alumina, followed by calcination (eq. 1). Cu/Al₂O₃ catalyzed the oxidative degradation of 1,3-dihydroxyacetone with hydrogen peroxide in water to give glycolic acid in 91% yield with co-production of formic acid (eq. 2). The reaction also proceeded in the presence of amines or alcohols to afford the corresponding formamides or formates as co-products in 70–99% yield (eq. 3).

**Comment:** In the oxidation of 1,3-dihydroxyacetone, Cu/Al₂O₃ was recovered by centrifugation and reused twice without loss of its catalytic performance (fresh: 91% yield; third run: 88%). ICP analyses and a filtration test suggested that the reaction proceeds heterogeneously. XRD, HAADF-STEM, and N₂ adsorption–desorption experiments on the reused catalyst showed no obvious changes in its structure.

**Selected examples:**

- **R₁ = n-Bu, R₂ = n-Bu**
  - 99% yield

- **R₁ = n-C₄H₉, R₂ = n-C₄H₉, R₃ = H**
  - 98% yield

- **R₁ = Cl, R₂ = H**
  - 97% yield

- **R₁ = Me, R₂ = H**
  - 95% yield

- **R₁ = OCH₃, R₂ = Br**
  - 85% yield

- **R₁ = OMe, R₂ = n-Hex**
  - 96% yield