A continuous diethanolamine dehydrogenation fixed bed catalyst and reactor system

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HIGHLIGHTS

- A Cu/Co/ZrO$_2$ catalyst enables continuous production of disodiumiminodiacetic acid.
- Yields of 98% are achievable in a series of adiabatic trickle beds.
- Laboratory tests should be conducted under commercially representative conditions.

ARTICLE INFO

ABSTRACT

We have developed a fixed bed Cu/Co/ZrO$_2$ catalyst and reactor system for the production of disodiumiminodiacetic acid by dehydrogenation of diethanolamine. This process can give high molar yields (>98%) in a series of adiabatic reactors with interstage heating. This research and development program proceeded in three stages: catalyst discovery, reactor design, and process development. The discovery of a catalyst formulation that is superior in activity and selectivity to sponge-metal copper enabled project success. Subsequent reactor scale-up proceeded based on laboratory scale measurements of the reaction kinetics and catalyst lifetime. Validation experiments demonstrated the importance of using feed compositions and operating conditions in the laboratory that are identical to those expected in the full-scale operation.

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1. Introduction

The effectiveness of glyphosate, perhaps the best known herbicide, was initially discovered by Monsanto, and this product was first launched in 1974. Typically formulated as the highly water soluble isopropylamine salt, glyphosate is a systemic, non-selective, and broad-spectrum herbicide that is effective for over 300 weed species and is used to protect more than 100 different crops. We have developed alternative continuous process technology [1] for the production of glyphosate, the largest volume commodity agricultural chemical.

One key reaction step in our alternative, cost-efficient route for glyphosate synthesis is the dehydrogenation of diethanolamine (DEA) to form disodiumiminodiacetic acid (DSIDA or IDA). Early process technology utilized a sponge-metal copper catalyst in a slurry reactor [2]. To reduce processing costs, we sought to develop a continuous fixed bed process that would provide long catalyst lifetime, high DEA conversions, and high DSIDA selectivities, eliminat-

ing the operational costs associated with catalyst attrition, catalyst recovery, and catalyst recycle using slurry reactor technology and increasing the operational efficiency relative to slurry-based batch processing. In this summary of our development program, we highlight key findings while reviewing the scale-up methodology.

Scheme 1 illustrates the overall reaction for the dehydrogenation of DEA. The reaction is endothermic (estimated at 12 kcal/mol DEA) and gives reasonable reaction rates and selectivities at temperatures between 140 and 200 °C. This overall reaction is believed to involve at least two mechanistic steps: (a) dehydrogenation of the alcohol to form an aldehyde intermediate [3] and (b) further oxidation of the aldehyde to the final product. These two reaction steps occur with both of the alcohol groups on the DEA molecule, resulting in net production of four moles of hydrogen gas per mole of DEA converted. In our experiments, described later, we observed no aldehyde intermediate. This observation is consistent with the initial dehydrogenation (formation of the aldehyde intermediate) being the rate-limiting step.

The primary reaction byproduct observed in the experimental work was the sodium salt of hydroxyethylglycine (HEG), which is formed when only one of the alcohol groups in DEA is converted to the acid functionality as illustrated in Scheme 2. Thus, HEG is the

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intermediate in a series reaction. Other potential byproducts include the sodium salts of glycine (aminoacetic acid), glycolic acid, and oxalic acid. The selectivity to glycine is small but significant at high conversions of DEA. Because the yield loss to glycine may affect the process economics, our efforts to develop a kinetic model included the conversion of DSIDA to the sodium salts of glycine (GLY) and oxalic acid (OXA) according to the following stoichiometry:

$$DSIDA + NaOH + H_2O \rightarrow GLY + OXA + 2H_2 \qquad (1)$$
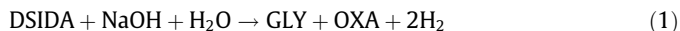
We observed low levels of glycolic acid in some experiments. Presumably, each mole of glycolic acid is formed in conjunction with a mole of glycine as shown in Scheme 3. Further dehydrogenation of the glycolic acid then yields oxalic acid, giving the overall reaction represented by Eq. (1).

2. Materials and methods

This research and development program proceeded in three stages: catalyst discovery, reactor design, and process development. The catalyst discovery phase employed a batch slurry reactor for screening alternative catalyst materials. The reactor design work employed continuous laboratory scale trickle bed experiments over a range of compositions and temperatures. The resulting kinetic model, combined with the energy balance equation for an adiabatic plug flow reactor, provided the basis for designing the envisioned full-scale reactor system. Finally, various process development experiments guided further process refinements and validated earlier assumptions. These experiments included catalyst lifetime tests in a laboratory scale trickle bed reactor. This section provides the experimental details for the two different laboratory reactor systems.

### 2.1. Batch slurry stirred tank reactor

Initial catalyst screening experiments employed a batch slurry reactor. The reactor was a mechanically agitated 600 mL Parr reactor made of HASTELLOY® C. After initial tests with a sponge-metal
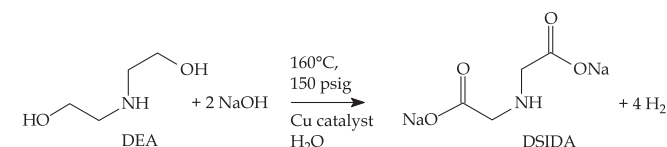
Scheme 1. Overall stoichiometry for DEA dehydrogenation reaction chemistry.
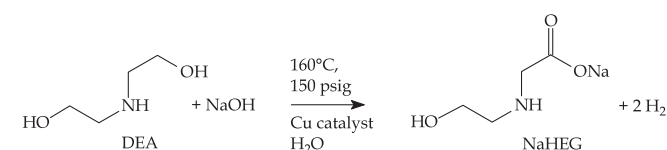
Scheme 2. Intermediate formation stoichiometry for DEA dehydrogenation reaction chemistry.
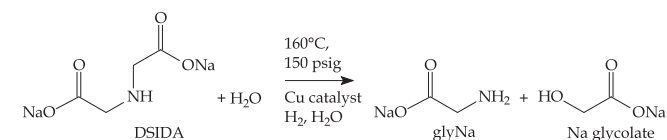
Scheme 3. Glycine formation stoichiometry for DEA dehydrogenation reaction chemistry.

(generic Raney™) copper catalyst to validate the reactor performance, we tested various copper-containing formulations in isothermal experiments with 25 wt% DEA in an aqueous solution with 2.1 equiv. of NaOH and typically 0.16 equiv. of Cu at temperatures from 160 to 230 °C. We operated the reactor as a closed system, with the pressure rising until an upper limit of 400–700 psig, at which time we vented the byproduct hydrogen from the reactor until reaching 150–200 psig, thereafter allowing the pressure to rise again. In a typical experiment, we vented the reactor two or three times.

We tested four different types of copper catalysts: sponge-metal copper, copper chromites, a methanol synthesis catalyst, and a few reductive amination catalysts (Table 1). Except for the sponge-metal copper, we reduced all catalysts from the stable oxide (CuO) with more than three molar equivalents of hydrogen in a stream containing 10% hydrogen in nitrogen at 200 °C over about 24 h in a quartz tube. We typically purged the reactor headspace with nitrogen prior to the addition of the catalyst to minimize oxide formation during the transfer from the quartz tube.

In a typical experiment, we charged the reactor with 50 g (0.49 mol) of diethanolamine, 82 g of 50% solution in water of sodium hydroxide (1.03 mol), and 68 g of water. We then added 2–10 g of a powdered catalyst. After the addition of catalyst to the reactor, we heated the reaction mixture to 160 °C with stirring. The hydrogen typically began to evolve at about 140 °C, indicating the onset of the dehydrogenation reaction. We easily detected completion of the reaction by monitoring the pressure rise. Depending on the catalyst load and activity, total batch times ranged from 40 to 600 min. Subsequently, we cooled and analyzed the mixture by high pressure liquid chromatography (HPLC). We analyzed for impurities by gas chromatography, and we occasionally employed ^{13}C nuclear magnetic resonance (NMR).

2.2. Continuous fixed bed reactor

Based on reports in the open literature [4,5], diluting a lab scale multiphase fixed bed with fines is effective at decoupling the kinetic behavior of the catalyst pellets from the reactor hydrodynamics. These two reports show that cocurrent upflow and downflow lab scale reactors give identical results when the catalyst is diluted with fines. With sufficiently high liquid feed rates, the inert fines give essentially complete wetting (irrigation) of the catalyst particles and make external transport resistances negligible. Thus, reaction kinetic models derived from these lab scale studies are applicable to the design, optimization, and control of commercial scale reactors, which will also operate with complete wetting and no external transport resistances.

Consequently, the continuous fixed bed laboratory reactor for DEA dehydrogenation operated in cocurrent downflow (trickle flow). Silicon carbon fines (80–100 mesh, or about 200 μm in diameter) diluted the 5–28 g of catalyst (as oxides) in a ratio of 0.6 to 1:1 by mass. For all catalyst loads, between 16 and 25 g of additional SiC were loaded above and below the catalyst bed to promote liquid radial distribution before the catalyst zone and to position the catalyst zone within the jacketed portion of the reactor tube.

The reactor (Fig. 1) consisted of a 1/2-inch HASTELLOY® C tube (inner diameter of 0.43 inches) with a jacket containing circulating heat transfer oil. We chose the catalyst bed length to be sufficiently long to satisfy the plug flow performance criterion at reasonably high DEA conversions [6–8]. Similarly, we selected the tube inner diameter to satisfy the isothermal criterion by Mears [9]. An oil bath thermostatically controlled and circulated the oil. Insulation on all oil lines reduced heat loss. A thermocouple positioned just below the bottom of the catalyst bed along the reactor axis independently monitored the reactor temperature. A Gilson model