

Continuous Reductive Hydroformylation in a Segmented Slug Flow Reactor Using a Single Catalyst Enabled by CO-Degassing

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Higher alcohols are widely used as components for surfactants, lubricants, solvents, and plasticizers and are typically produced via heterogeneous hydrogenation of aldehydes. However, this often requires harsh reaction conditions. A more sustainable approach would be a tandem reaction, where both hydroformylation and aldehyde reduction occur under similar homogeneous conditions, reducing environmental impact.

Rhodium catalysts, known for their reducing properties in hydroaminomethylation, have the potential to efficiently catalyze this tandem process. However, carbon monoxide (CO) strongly inhibits aldehyde reduction, even at low concentrations. To overcome this challenge, existing tandem systems typically employ multiple catalysts, use significantly different reaction conditions for each step, or incorporate highly reactive monodentate alkylphosphine ligands, which in turn result in the formation of undesired branched alcohols.

We hypothesize that efficient CO removal after hydroformylation could enable conventional hydroformylation catalysts to facilitate reductive hydroformylation under otherwise similar conditions for both steps. To investigate this, we developed a continuous flow system. First, we studied CO inhibition and identified a suitable tube-in-tube capillary degassing technique. This setup was then integrated into a continuous flow reactor, where 1-octene undergoes hydroformylation, followed by the removal of residual syngas. Subsequently, hydrogen is introduced, enabling the hydrogenation of nonanal to nonanol under otherwise identical reaction conditions (Figure 1).

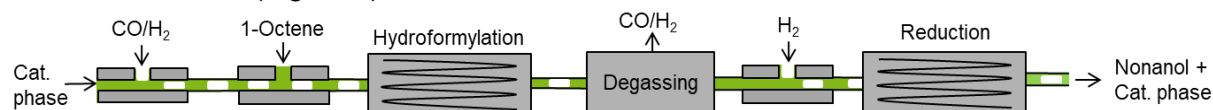


Figure 1: Schematic illustration of the continuous flow set-up.

In our feasibility study, the first-ever continuous reductive hydroformylation system with integrated CO degassing demonstrated a fourfold increase in alcohol formation compared to reactions without CO removal. The system also achieved higher product linearities and yields of up to 80%, outperforming many methods reported in the literature - even without optimization.

We expect that with further optimization and a more comprehensive kinetic and catalytic understanding, this approach could pave the way for a more efficient and sustainable alcohol synthesis process.