

## Exploiting CO<sub>2</sub>-Expanded Liquids in Hydroformylation: A Molecular Simulation Approach

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We present calculations of the phase equilibrium and transport properties of CO<sub>2</sub>-expanded liquids (CXLs) in hydroformylation *via* Monte Carlo and molecular dynamics (MD) simulations. Gibbs ensemble Monte Carlo simulations were performed to determine the volume expansion, pressure-dependent composition, and pressure-density phase diagrams. MD simulations were conducted to compute the transport properties of the CXLs. The motivation for this study is the use of simple homogeneous Rh/TPP catalyst for 1-octene hydroformylation in CO<sub>2</sub>-expanded liquid media, which provides exceptional turnover frequency (TOF) and regioselectivity at mild pressure and temperature compared to conventional Co-based process. In general, higher H<sub>2</sub> concentrations are needed for catalyst activation and lower CO concentrations are required to avoid rate inhibition due to the formation of inactive carbonyl species. Because, CO is generally more soluble than H<sub>2</sub> in most conventional solvents, the resulting H<sub>2</sub>/CO ratio in the liquid phase is less than that in the feed syngas. In contrast, when dense CO<sub>2</sub> is added to either 1-octene or nonanal at a fixed syngas partial pressure, H<sub>2</sub> becomes more soluble than CO in the generated CXLs, giving rise to greater H<sub>2</sub>/CO ratios. This unique tunability of the H<sub>2</sub>/CO ratio in CXL media (*i.e.*, without having to change the syngas feed composition) is believed to enhance both TOF and *n/i* ratio. However, the underlying molecular-level understanding of this system is lacking. Therefore, the aim of this study is to provide new insight that could help to optimize the syngas ratio in the solvents involved in the hydroformylation reaction.

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