

Homogeneous Olefin Hydroformylation by Transition Metal Complexes in CO₂-Expanded Media: Solvent Effects and Kinetics

Jing Fang^{1,2}, Debangshu Guha^{2,3}, Jon A. Tunge^{2,4}, Milorad Dudukovic,^{2,3} P. A. Ramachandran^{2,3} and Bala Subramaniam^{1,2,*}

¹Department of Chemical and Petroleum Engineering, ²Center for Environmentally Beneficial Catalysis (CEBC), ⁴Department of Chemistry, University of Kansas, Lawrence, KS 66045

³Department of Chemical, Energy and Environmental Engineering, Washington University in St. Louis, St. Louis, MO 63130

*bsubramaniam@ku.edu

Introduction

In recent years, investigations in CEBC laboratories and elsewhere [1, 2] have clearly demonstrated how a relatively new class of solvents, called CO₂-expanded liquids (CXLs), are promising alternative media for performing catalytic reactions. CO₂-expanded liquids (CXLs), are generated by mixing dense CO₂ with traditional solvents to yield a new liquid phase (called the CXL phase). The CXL properties (such as transport coefficients and dielectric constant) are easily tuned by CO₂ addition to accommodate contrasting solubilities simultaneously: a large amount of CO₂ enhances permanent gas solubility and the organic solvent favors metal catalyst solubility. Recently, CEBC researchers reported a novel process that exploits CXLs to intensify hydroformylation reactions [3]. For 1-octene hydroformylation on Rh(acac)(CO)₂ modified by biphephos ligand, turnover frequency (~300 h⁻¹) and the selectivity towards the linear aldehyde (~90%) are significantly enhanced in CXLs relative to the reaction in neat media. Further, these enhancements occur at milder pressures (~40 bar) and temperatures (60°C). In this work, we present detailed kinetic modeling of the hydroformylation reactions in various solvent media including CXLs, aimed at a better fundamental understanding of the underlying physicochemical processes.

Materials and Methods

1-olefin hydroformylation on Rh and Co complexes were investigated in neat solvents and in CXLs using a 50-cm³ high-pressure autoclave reactor equipped with an *in situ* attenuated total reflectance (ATR) IR probe (Mettler Toledo Inc.). Syngas is introduced from a gas reservoir such that constant total pressure is maintained in the reactor. The common experimental conditions are as follows: T = 60°C; CO:H₂ = 1; Octene/Rh = 2168. For experiments with neat solvents, the syngas pressure is 20 bar. For experiments with CXLs, the syngas and CO₂ partial pressures are 6 bar and 32 bar, respectively. Details of the mathematical models may be found elsewhere [4]. An orthogonal distance regression technique was used to obtain the kinetic parameters from the temporal ReactIR concentration profiles.

Results and Discussion

Based on the kinetic scheme presented by Evans et al. [5], the kinetic parameters for the key catalytic steps of catalyst hydrogenation (k_1), nonanal formation (k_4) and octene isomerization (k_8) were obtained in the various solvents. The estimated kinetic constants are compared in Table 1. Good matches were confirmed between the experimental profiles and those predicted using the regressed parameters (see Figures 1 and 2 for the matches in CXLs).

Table 1. Comparison of rate constants

Rate constants	Neat Octene	CXLs
k_1 (m ³ mol ⁻¹ s ⁻¹)	4.41 (10 ⁻⁶)	1.25 (10 ⁻⁴)
k_4 (m ³ mol ⁻¹ s ⁻¹)	8.69 (10 ⁻⁴)	2.30 (10 ⁻³)
k_8 (s ⁻¹)	1.95 (10 ⁻⁶)	6.53 (10 ⁻⁶)

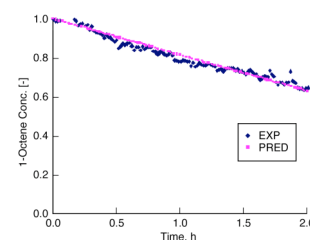


Figure 1. Experimental and predicted reactant concentrations in CXL media

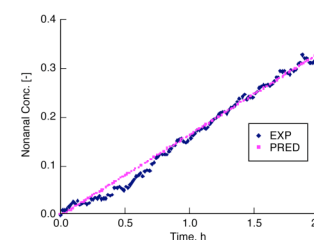


Figure 2. Experimental and predicted product concentrations in CXL media

As inferred from Table 1, the rate constant of the catalyst hydrogenation step (k_1) in CXLs is two orders of magnitude greater in CXLs than in neat 1-octene. Similarly, the rate constant for the product formation step (k_2) is one order of magnitude greater in CXLs than in 1-octene. We had previously observed that the reaction induction period is on the order of tens of minutes in 1-octene and only a few minutes in the case of CXLs [4]. However, regression of the concentration profiles beyond the induction period did not change the relative magnitudes of the regressed rate constants. These results are unprecedented and imply a rather strong solvent effect on the hydroformylation rate constants. Systematic investigations are being undertaken aimed at understanding possible solvent effects on the hydroformylation reaction mechanism and kinetics. These results will be presented and discussed at the meeting.

Significance

CXLs intensify hydroformylation rates at mild pressures (tens of bars) and temperatures (<100°C) compared to industrial hydroformylation processes, which require harsher pressures (> 100 bars) and temperatures (> 150°C). The use of CXLs is therefore of practical interest. This contribution will shed fundamental insights into the mechanism and kinetics of catalytic hydroformylation in tunable CXL media.

References

1. Wei, M., Musie, G.T., Busch, D.H. and Subramaniam, B. *J. Am. Chem. Soc.* 124, 2513 (2002).
2. Jessop, P.G.; Stanley, R.R.; Brown, R.A.; Eckert, C.A., Liotta, C.L., Ngo, T.T., and Pollet, P. *Green Chem.* 5, 123 (2003).
3. Jin, H., Ghosh, A., Tunge, J.A. and B. Subramaniam, B. *AIChE Journal* 52, 2575 (2006).
4. Guha, D., Jin, H., Dudukovic, M.P., Ramachandran, P.A. and Subramaniam, B. *Chemical Engineering Science* (in press).
5. Evans, D., Osborn, J.A. and Wilkinson, G. *Journal of Chemical Society (A): Inorganic, Physical and Theoretical* 3133 (1968).