

Kinetics of Cinnamaldehyde Hydrogenation in Four Phase System

Muzammil Khan¹, Sunil Joshi^{1*}, Vivek Ranade²

¹Chemical Engineering and Process Development Division, National Chemical Laboratory, Pune, India

²School of Chemistry and Chemical Engineering, Queen's University, Belfast, Northern Ireland, UK

*Corresponding author: ss.joshi@ncl.res.in

Highlights

- Kinetics of Cinnamaldehyde hydrogenation in Gas-Liquid-Liquid-Solid system was studied.
- The Langmuir-Hinshelwood kinetic model with surface reaction as limiting step was used.
- Thermodynamic model for solubility was incorporated with this kinetic model.
- Fourth phase (aqueous alkali) increases selectivity towards unsaturated alcohol.

1. Introduction

Hydrogenation reactions carried out in four phase systems bring in additional benefits in terms of selectivity and separation of desired product [1-2]. In this study, Cinnamaldehyde hydrogenation was carried out in a batch system comprising of phases- gas (Hydrogen), organic liquid (Cinnamaldehyde + Toluene), aqueous liquid (alkali solution) and solid (5% Pt/C catalyst). The catalyst was present in organic phase. The addition of aqueous alkali increases selectivity towards unsaturated alcohol (Cinnamyl Alcohol) as reported by various authors [3-5]. After establishing operating conditions for kinetic regime, the effect of temperature, pressure, catalyst loading, initial concentration of Cinnamaldehyde, concentration of alkali on initial rate of reaction was investigated. Langmuir-Hinshelwood type of kinetic model was proposed for evaluation of kinetic parameters. The experimentally obtained concentration vs. time profiles were used to obtain values of kinetic parameters. Hydrogen pressure being one of controlling parameters, the equilibrium solubility of Hydrogen in reaction mixture was estimated using a thermodynamic model [6] and this model was integrated with the kinetic model. The developed kinetic model will be useful for simulating Cinnamaldehyde hydrogenation reactor using four phase (GLLS) reactor model [7].

2. Methods

The experiments were carried out in a 50 ml stainless steel reactor in semi-batch mode (Hydrogen was fed as per consumption). The typical reaction feed consisted of Cinnamaldehyde 50% w/W in Toluene, KOH 17% w/W in water, 1% catalyst loading in organic phase and operating conditions ranged from Temperature, 303-323 K and Pressure, 10-30 Bar [8].

Reaction scheme for hydrogenation of Cinnamaldehyde:

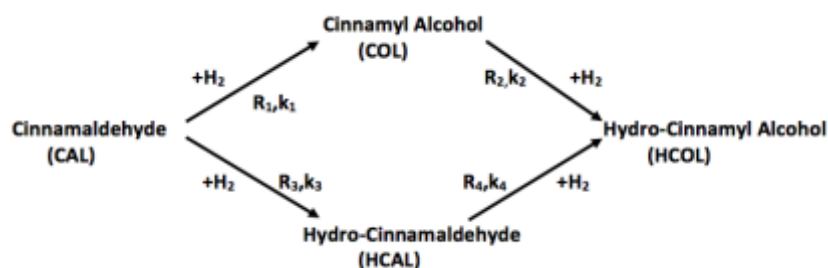


Fig.1 Reaction Scheme for hydrogenation of Cinnamaldehyde

Following rate equations were used in kinetic model:

$$R_1 = \frac{k_1 w (k_h P) [CAL]}{1 + K_{CAL} [CAL]}$$

$$R_2 = \frac{k_2 w (k_h P) [COL]}{1 + K_{COL} [COL]}$$

$$R_3 = \frac{k_3 w (k_h P) [CAL]}{1 + K_{CAL} [CAL]}$$

$$R_4 = \frac{k_4 w (k_h P) [HCAL]}{1 + K_{CAL} [CAL]}$$

Where k_1, k_2, k_3, k_4 are rate constants, K_{CAL} and K_{COL} are adsorption coefficients, w is catalyst loading, k_h is Henry's Constant, P is pressure.

3. Results and discussion

The concentration vs time profile from model results were plotted against experimental data at $T=313$ K.

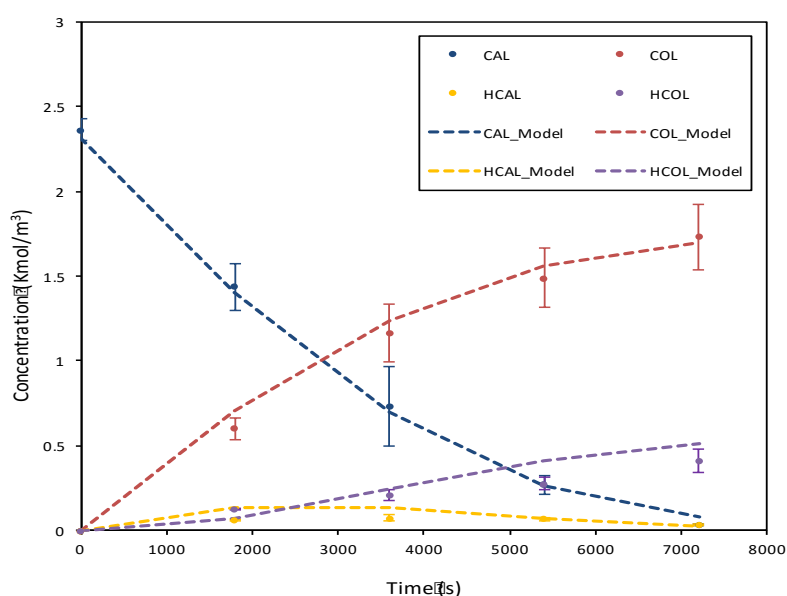


Fig.2 Model results vs Experimental data at $T=313$ K, $P=20$ Bar, 1% catalyst loading in organic phase.

4. Conclusions

The rate constants, adsorption coefficients calculated at $T=303, 313, 323$ K were used to determine activation energies for individual reactions. The proposed kinetic model was shown to describe the experimental data well. The model will be useful for simulation and optimization of Cinnamaldehyde hydrogenation reactor.

References

- [1] C.V. Rode, M.J. Vaidya, R.Jaganathan, R.V. Chaudhary, Chemical Engineering Science 56(2001) 1299-1304.
- [2] F. Dobert, J. Gaube, Catalysis Letters, 1995, 31,431-438.
- [3] L.J. Durndell, C. M. A. Parlett, N.S. Hondow, M. A. Isaacs, K. Wilson, A.F. Lee, Nature Scientific Reports, 2015, Sci. Rep. 5, 9425.
- [4] V. Ponc, Applied Catalysis A: General 149 (1997) 27-48.
- [5] H. Yamada, H. Urano, S. Goto, Chemical Engineering Science 54 (1999) 5231-5235.
- [6] Purwanto, R.M. Deshpande, R.V. Chaudhari, H. Delmas, J. Chem. Eng. Data 1996, 41, 1414-1417.
- [7] D.V. Sharma, A.W. Patwardhan, V.V. Ranade, Ind. Eng. Chem. Res., 2017, 56 (6), pp 1404–1415
- [8] A.M. Garkhedkar, S.K. Shingote, V.H. Rane, A.A. Kelkar, V.V. Ranade, Indian Chemical Engineer, 2015, 57:3-4, 219-239.

Keywords

Kinetics, Four phase system, thermodynamic model.