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Kinetics of Cinnamaldehyde hydrogenation in four phase system

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Abstract:

The kinetics of cinnamaldehyde hydrogenation in four phase system viz. gas (hydrogen)-liquid (cinnamaldehyde + toluene)-liquid (aqueous KOH)-solid (catalyst, 5% Pt/C), [GLLS] system has been studied in this work. As reported, addition of aqueous alkali in hydrogenation of unsaturated aldehydes like cinnamaldehyde shifts selectivity towards unsaturated alcohol, cinnamyl alcohol. The promotion action by alkali metals for improving selectivity towards cinnamyl alcohol involves changes in the adsorption mechanism of the cinnamaldehyde in a way that C=O bond get preferentially hydrogenated. In cinnamaldehyde hydrogenation in presence of promoters two different catalytic sites can be considered, each for C=O and C=C bond hydrogenation. In accordance with this consideration and as demonstrated in various studies on hydrogenation of unsaturated aldehydes, further hydrogenation of intermediate-cinnamyl alcohol (C=C bond hydrogenation) occurs on Pt only sites while cinnamaldehyde and intermediate hydrocinnamaldehyde (both involving C=O bond hydrogenation) are hydrogenated on catalytic

sites affected by promoters. This preferential adsorption and hydrogenation through C=O bond leads to the increased selectivity of cinnamyl alcohol. Although, many authors have studied cinnamaldehyde hydrogenation using various promoters, there are very few reports on kinetics in which this two site approach behind promotion action has been considered. The effect of various operating parameters on the rates of hydrogenation was studied and the two site Langmuir-Hinshelwood type of kinetic model was used for evaluating the kinetic parameters by fitting experimental data. The thermodynamic model for estimating the solubility of hydrogen in the reaction mixture was incorporated with this kinetic model.

Keywords: Kinetics, four phase system [GLLS], promoters, Langmuir-Hinshelwood kinetic model.

Introduction:

The catalytic hydrogenation processes are one of the most used processes in the fine and specialty chemical industry. Hydrogenation reactions have broad spectrum of applicability with an abundance of opportunities for chemo and stereo-selectivity. Heterogeneous catalytic hydrogenation processes have advantage over homogenous hydrogenations in terms of catalyst separation on the conclusion of the hydrogenation process. Rylander et al.[1] have extensively reviewed the catalytic hydrogenation processes providing useful guidelines for selection of catalyst, operating conditions, solvent and generalizing the approach for hydrogenation of specific functional groups. Different functional groups in multi-functional compounds can

compete for hydrogenation giving multiple products by hydrogenation of these functional groups.

In case of hydrogenation of α,β - unsaturated aldehydes, reduction of C=C bond gives saturated aldehydes while saturated alcohols are formed on C=O bond reduction. The hydrogenation of the C=C bond is easy compared to reduction of C=O bond, as C=C bond hydrogenation is favored thermodynamically[2]. The unsaturated alcohols find great application in the fine chemicals production especially in the field of flavors and fragrance industry[3,4]. This implies the necessity for thorough study for different aspects affecting the selectivity of hydrogenation products of α,β - unsaturated aldehydes. Various authors have reviewed the different selectivity aspects for hydrogenation of unsaturated aldehydes[1,2,5–13]. In general, hydrogenation of unsaturated aldehydes using platinum as catalyst gives unsaturated alcohols as the major product while use of palladium catalyst produces majorly saturated aldehydes[1]. The presence of more electropositive metal or metal oxide favors hydrogenation of the C=O bond[2,7]. The steric effects can affect the adsorption inclination of the substrate species on the catalysts hindering the C=C bond hydrogenation[2,6].

Cinnamaldehyde, an α,β - unsaturated aldehydes is used for manufacturing cinnamyl alcohol which finds applications in perfume and flavoring industry, conventionally it is manufactured by using stoichiometric reagent based synthesis producing considerable waste per unit mass of product formed. Considering the necessity of environmentally benign process for manufacturing cinnamyl alcohol and the challenges involved in increasing selectivity towards unsaturated alcohols in hydrogenation of unsaturated aldehydes, extensive research has been done on selective hydrogenation of cinnamaldehyde. Breen et al.[6] have studied the steric effects in cinnamaldehyde hydrogenation on graphite supported iridium catalyst. As reported, due to the

strong adsorption of the cinnamyl alcohol on Ir/C catalyst surface creates steric effects inhibiting its further hydrogenation to hydrocinnamyl alcohol. Whereas hydrocinnamaldehyde is readily hydrogenated to hydrocinnamyl alcohol. Also, adding recycled stream of cinnamyl alcohol to the reaction feed greatly decreased hydrogenation of C=C bond. Similar selectivity aspects for cinnamaldehyde hydrogenation have been demonstrated by various authors using different catalysts viz. Pt/C[14], Pt/SiO₂[9], Pt/graphite and Pt/graphite-cobalt alloy catalyst[10], Pt nanoparticles[13], Pt/C/monolithic catalyst[15], alumina supported ruthenium[16], supported ionic liquid catalysts[17], Cu-based catalysts[18] etc. Galvagno et al.[11] have reported use of metal chlorides like FeCl₃, SnCl₄, GeCl₄ for promoting selectivity towards cinnamyl alcohol.

Most of the reports on the kinetics of the cinnamaldehyde hydrogenation on different catalysts have used Langmuir-Hinshelwood type of kinetic model for fitting the experimental data, with variations for incorporating the increased selectivity towards cinnamyl alcohol. For example, in the work by Tronconi et al.[19], kinetic model considering two different catalytic sites on Pt-Sn/nylon catalyst have been used. With Pt-Sn catalytic sites associated with hydrogenation of cinnamaldehyde and hydrocinnamaldehyde while Pt only catalytic sites for hydrogenation of cinnamyl alcohol. In other words, the promoter affected catalytic sites are involved in the hydrogenation of C=O bond while Pt only sites are associated with C=C bond hydrogenation. This adsorption and hydrogenation of C=C and C=O groups have been explained by Neri et al.[16] for cinnamaldehyde hydrogenation over alumina-supported ruthenium catalyst. The authors have reported that on the ruthenium metal particles having different size, the substrate is chemisorbed with a different geometry. Similar two site mechanism has been reported for unsaturated aldehyde substrates, like 2-methyl-2-pentenal hydrogenation over Raney cobalt

catalyst by Hotta et al.[20] and for 2-ethyl-2-hexenal hydrogenation on Ni/SiO₂ catalyst by Niklasson et al.[21].

The addition of the aqueous alkali together with the reaction mixture of cinnamaldehyde hydrogenation has shown to increase the selectivity towards cinnamyl alcohol[7,10,12,14,22], this leads to the formation of gas-liquid-liquid-solid, GLLS system. This promotion action by alkali cations can be explained on the grounds of two site adsorption mechanism. Yamada et al.[22] have reported zero order kinetics for cinnamaldehyde hydrogenation using Pt/C catalyst and aqueous KOH solution as promoter. But not all kinetic parameters are reported in this study. The power law kinetic approach cannot adequately explain kinetics of surface catalyzed reaction as elaborated by Kumar et al.[23]. This implies the necessity of thorough kinetic study for hydrogenation of cinnamaldehyde in four phase system explaining the adsorption mechanisms involved and its consequent effect on overall rate of hydrogenations and selectivity.

In this work the cinnamaldehyde hydrogenation on the 5% Pt/C catalyst was studied in the presence of aqueous KOH as promoter making this a gas (hydrogen), liquid (toluene + cinnamaldehyde), liquid (aqueous), solid (catalyst), [GLLS] system. The hydrogenation reaction occurs in the organic phase as catalyst is present in the organic liquid phase. Toluene was selected as solvent for this hydrogenation because of high hydrogen solubility in toluene[24,25], high catalytic activity and increased selectivity towards obtained cinnamyl alcohol compared to other solvents[14]. The effect of various operating parameters on the initial rates of hydrogenation, conversion and selectivity was studied. The catalyst loading, partial pressure of hydrogen and initial substrate concentration were found to be the parameters controlling the rates of hydrogenation. The experimental batch reaction data was fitted using Langmuir-Hinshelwood

type kinetic model assuming two catalytic sites. The kinetic model results are compared with experimental batch reaction data and results from previous study[22] reporting the kinetics for cinnamaldehyde hydrogenation in four phase system. The thermodynamic model for predicting the solubility of hydrogen in biphasic reaction mixture was incorporated with this kinetic model.

Reaction mechanism:

Figure 1 shows the reaction scheme for cinnamaldehyde hydrogenation in the four phase system.

Figure 1: Reaction scheme for cinnamaldehyde hydrogenation in four phase system

The hydrogenation of the C=C and C=O bonds in cinnamaldehyde gives hydrocinnamaldehyde (HCAL) and cinnamyl alcohol (COL)(desired product), respectively. Both hydrocinnamaldehyde and cinnamyl alcohol are further hydrogenated to produce hydrocinnamyl alcohol (HCOL), a

saturated alcohol. The addition of the aqueous KOH solution with reaction mixture inhibits the hydrogenation of cinnamaldehyde to hydrocinnamaldehyde (forward reaction path, R_2) and cinnamyl alcohol to hydrocinnamyl alcohol (forward reaction, path R_4) to great extent increasing selectivity to cinnamyl alcohol, as elaborated later in kinetic model part. Other intermediates are also formed in trace amounts like β -methylstyrene and phenylpropane.

Experimental Setup and Procedure:

Solubility of hydrogen in reaction mixture:

The effect of change of hydrogen concentration in reaction mixture with respect to temperature, pressure and composition of the reaction mixture was determined in terms of solubility of hydrogen ($\text{kmol.m}^{-3}.\text{MPa}^{-1}$) in the reaction mixture. The solubility of hydrogen in a given liquid was calculated using pressure drop method. Jauregui-Haza et al.[25] and Purwanto et al.[26] have used this method for determining solubility of hydrogen in water and various organic solvents.

The experimental setup for determining solubility of gases in liquid is similar to batch reaction setup (**Figure 2**). In a typical experiment, $2 \times 10^{-4} \text{ m}^3$ of the reaction mixture (without the catalyst) was degassed to remove the dissolved air and the overhead space of autoclave was flushed with hydrogen. Once the desired temperature of the mixture is attained, the gas was fed to the overhead space of an autoclave until the desired value of pressure (set value) is reached. The isothermal condition at this temperature was maintained using heating-cooling setup of the autoclave. The dip tube of the autoclave (notation 8, **Figure 2**) which passes gas directly into the liquid was removed prior to the experiment. Once the set value of pressure is reached, the stirrer

of autoclave was started and gas is dissolved into the liquid until the equilibrium is reached. The change in pressure of the autoclave was recorded with respect to time. From the difference between the set and equilibrium pressure values, the number of moles of hydrogen dissolved into the liquid at the given temperature and equilibrium pressure can be calculated using equation of state for gases. The partial pressure of hydrogen was considered in these calculations taking into account the vapor pressure of the solvent. While passing the gas in the overhead space of the autoclave, the optimum flow rate of $0.02\text{-}0.04\text{ MPa}\cdot\text{sec}^{-1}$ was maintained, so that the gas should not pass directly into the bulk liquid. The solubility of hydrogen was determined in the reaction mixtures containing different ratios of organic/inorganic liquid volume in the temperature range of $298\text{-}353\text{ K}$. The solubility values were reported as Henry's constants [$\text{kmol}\cdot\text{m}^{-3}\cdot\text{MPa}^{-1}$].

Cinnamaldehyde Hydrogenation:

Batch reactions were performed in a $5 \times 10^{-5}\text{ m}^3$ autoclave (Parr Instruments Ltd. USA) in the temperature range of $303\text{-}323\text{ K}$ and $1\text{-}3\text{ MPa}$ pressure using 5% Pt/C catalyst. The autoclave was equipped with a 4 blade impeller which has 60% diameter of vessels inside diameter, sampling valve and heating-cooling arrangements with PID controller for isothermal operation. The particle size of the catalyst was in the range of $2\text{-}5\text{ }\mu\text{m}$. **Figure 2** shows the experimental batch setup for cinnamaldehyde hydrogenation.

Figure 2: Experimental Setup for batch cinnamaldehyde hydrogenation

In a typical experiment 0.3 w/W cinnamaldehyde in toluene was fed to the autoclave together with 3 M aqueous KOH solution. The organic volume was 75% of the total reaction mixture volume (~25 ml). The catalyst 5% Pt/C was added to the reaction mixture with catalyst loading of 1% w/W of the total reaction mixture, the catalyst was present in the organic phase. The overhead space of the autoclave was purged with hydrogen to remove the air. After the desired temperature was attained the hydrogen gas was fed to the autoclave through the dip tube until desired pressure is reached. The isothermal conditions are maintained at this temperature using heating-cooling arrangements of the autoclave and PID controller. The reaction mixture was stirred continuously at high RPM (~1400) to remove mass transfer limitations between phases and ensure kinetic regime of operation. The reduced hydrogen pressure was recovered periodically as hydrogen is consumed as reaction proceeds.

Samples were taken periodically from the sampling valve (notation 9, **Figure 2**) connected to the dip tube, under constant stirring for total 3 hours of reaction time. The samples were analyzed

using the gas chromatography. The batch reactions were repeated multiple times for same operating conditions and average values are reported.

Results and discussion:

Solubility of hydrogen:

The thermodynamic model developed by Prausnitz et al.[27] have been used to predict the solubility of hydrogen in the reaction mixture for cinnamaldehyde hydrogenation. The model has been proven to adequately predict the solubility of the gases in non-polar liquids as demonstrated by various authors [25,28,29] by applying model to different gas-liquid systems. This model explains two step approach involving condensation of gas to hypothetical liquid and its further dissolution in solvent using regular solution theory. The approach by Prausnitz et al.[27] was used to predict the solubility of hydrogen in pure toluene and cinnamaldehyde. The solubility of hydrogen in pure toluene was found to be more than twice of that in pure cinnamaldehyde. The solubility increased with temperature for both toluene and cinnamaldehyde. The model can be extended to solvent mixtures also. This extension applied to cinnamaldehyde and toluene mixtures predicted the hydrogen solubility in organic phase of the reaction mixture.

As stated earlier, this thermodynamic model is not applicable for the polar solvents. Lemcoff et al.[30] have studied the hydrogen solubility in polar solvents like acetone, isopropanol, methanol and water by applying Prausnitz et al.[27] model and comparing results with experimental data. Lemcoff et al.[30] have suggested the correction in evaluating the Hildebrand solubility parameter[31] for polar solvents. This approach by Lemcoff et al. [30] have also been used by

Radhakrishnan et al. [28] for estimating the solubility in methanol. The estimates reported by these authors seem to agree reasonably with the reported hydrogen solubility data in polar solvents. The approach by Prausnitz et al.[27], Lemcoff et al.[30] and Radhakrishnan et al.[28] was used to determine various parameters involved in this model applied to hydrogen-water system and predict hydrogen solubility in water. The solubility of hydrogen in water decreased with increasing temperature and was found to be less than 25% of the solubility in pure toluene.

To determine hydrogen solubility in aqueous KOH solution, the approach by Shoor et al. [32] was used. The decrease in the solubility of hydrogen in the water by addition of the KOH has been correlated by Shoor et al. [32]. This eventually lead to the estimation of the hydrogen solubility in the inorganic phase of the reaction mixture.

The volume fraction weighted solubility values in organic and inorganic liquid phases gave the hydrogen solubility values in the whole reaction mixture.

Figure 3 shows the comparison between reported[24,25], experimental data and model results for number of moles of hydrogen dissolved in per unit volume of toluene with respect to equilibrium pressure at different temperatures. As dissolved hydrogen forms a dilute solution with toluene, the Henry's law is followed, as can be seen in **Figure 3** the number of moles of hydrogen dissolved is proportional to the equilibrium pressure. The solubility of hydrogen in toluene increased with temperature. As evident from **Figure 3**, the experimental data is in good agreement with the literature data and model results.

Figure 3: Number of moles of hydrogen dissolved per unit volume of toluene w.r.t. equilibrium pressure at different temperatures, comparison of experimental, literature data[24,25] and model results.

Figure 4 shows the comparison between experimental data and model results for solubility of hydrogen in various compositions of reaction mixtures (different organic/inorganic liquid volume ratios) changing with temperature (organic phase has 0.3 w/W of cinnamaldehyde in toluene). Henry's constant, k_h decreased with decreasing organic/inorganic liquid volume ratio as hydrogen solubility is very less in water compared to that in toluene and cinnamaldehyde. Also, as the solubility of hydrogen in toluene and cinnamaldehyde increases with temperature while it decreases with temperature in case of water, the slope of lines in **Figure 4** can be seen decreasing with decreasing organic/inorganic liquid volume ratio.

Figure 4: Solubility of hydrogen in reaction mixture w. r. t. temperature with different ratios of organic/inorganic liquid volumes (organic phase- 0.3 w/W of cinnamaldehyde in toluene);
[Points- Experimental data, Continuous lines- Model predictions].

Effect of operating parameters:

Before determining the controlling parameters of the reaction kinetics, it is important to establish the kinetic regime of operation. To ensure that operating conditions for this batch operation are free from any mass transfer limitation, the batch reactions were performed at different rotating speeds of the impeller keeping other parameters constant. The catalyst activity at 15 min after start of the reaction increased for increasing RPM of the impeller up to 1000. Further increasing the RPM did not show any increment in the catalyst activity ($0.067 \text{ kmol.m}^{-3}.\text{sec}^{-1}.\text{gm}^{-1}$ for $>1000 \text{ RPM}$ at 323 K , 3 MPa). This implies that, that above RPM of 1000 the mass transfer

effects are not important. All the batch reactions were performed above 1000 RPM. The kinetic regime of operation is also evident from the linear increase of the rate with the catalyst loading discussed in next part. The intraparticle diffusion resistances were also assumed to be absent for very fine catalyst particles used in this study (2-5 μm).

Effect of catalyst loading:

The catalyst loading was changed in the range of 5-25 kg.m^{-3} at 313 K keeping all other operating conditions constant. As shown in **Figure 5** the rate of hydrogenation for all the species at 30 min after the start of the reaction increased with increasing catalyst loading. The rate of formation of cinnamyl alcohol almost doubled from 0.00025 to 0.00043 $\text{kmol.m}^{-3}.\text{sec}^{-1}$ for increasing catalyst loading from 5.8 to 23.6 kg.m^{-3} . The linear relationship between catalyst loading and rate of hydrogenation can be observed for all the species getting hydrogenated. This linear relationship verifies the kinetic regime of operation for the experiments performed, the operating conditions are adequate for eliminating the mass transfer limitations. The linear increment of the rate of hydrogenation with catalyst loading also justifies use of Langmuir adsorption isotherm (quasi-equilibrated adsorption of reactants) in rate expressions, as explained later in kinetic model part. The promotion action of aqueous KOH by preferentially hydrogenating C=O bond of cinnamaldehyde on Pt-K^+ catalytic sites is evident from the slope of plots in **Figure 5**, which is higher for cinnamyl alcohol (slope 1.0×10^{-5}) than hydrocinnamaldehyde (slope 8.3×10^{-7}), eventually increasing selectivity towards cinnamyl alcohol. The comparison of the relative increment in rate of formation with increased catalyst loading from 11.7 to 23.6 kg.m^{-3} for hydrocinnamaldehyde (23.4 %) and hydrocinnamyl alcohol (30.4%) also indicates increased promotion action by alkali, implying that at higher catalyst loading most of hydrocinnamyl alcohol getting formed is from hydrogenation of

hydrocinnamaldehyde (Reaction path, R₃ **Figure 1**) and cinnamyl alcohol is scarcely getting hydrogenated to hydrocinnamyl alcohol (Reaction path, R₄, **Figure 1**).

Figure 5: Initial rates of hydrogenation vs. catalyst loading at 313 K, 2 MPa pressure, 3 M KOH in aqueous phase, 0.3 w/W cinnamaldehyde in organic phase

Effect of substrate concentration:

The effect of initial concentration of cinnamaldehyde in toluene on the rates of hydrogenation was studied. As shown in **Figure 6** rates of hydrogenation at 30 min after start of reaction increased proportionally with increasing cinnamaldehyde concentration in organic phase in the range of 0.14 to 0.3 w/W. Further increasing the substrate concentration to 0.65 w/W decreased

the rates of hydrogenation to great extent. The solubility of hydrogen in cinnamaldehyde is $1.26 \times 10^{-2} \text{ kmol.m}^{-3}.\text{MPa}^{-1}$ while that in toluene is $3.05 \times 10^{-2} \text{ kmol.m}^{-3}.\text{MPa}^{-1}$ at 313 K. The observed decrease in rates of hydrogenation at high cinnamaldehyde concentration in organic phase (0.65 w/W) probably indicates the hydrogen starving of the cinnamaldehyde reaction mixture. As initial cinnamaldehyde concentration from 0.14 to 0.3 w/W was found to be optimum condition in terms of conversion and selectivity, batch experiments and kinetic studies were performed in this range.

Figure 6: Effect of changing initial substrate concentration on initial rates of hydrogenation at 313 K, 2 MPa pressure, 3 M KOH in aqueous phase, 12 kg.m^{-3} catalyst loading

Effect of hydrogen pressure:

The number of moles of hydrogen dissolved in reaction mixture is a direct function of partial pressure of hydrogen. Batch hydrogenations were performed in the pressure range of 1-3 MPa at 323 K keeping catalyst loading, KOH concentration and initial substrate concentration constant as the solubility of hydrogen in reaction mixture is dependent upon the composition of organic as well as aqueous phase. As shown in **Figure 7**, initial rates of hydrogenation at 15 min after start of reaction for substrate and intermediates increased with increasing partial pressure of hydrogen. From **Figure 7**, the increment in the initial reaction rate can be approximated by the linear relationship between the rate and partial pressure of hydrogen. In accordance with this observation, the term for number of moles of hydrogen dissolved per unit volume of reaction mixture ($k_h P_{H_2}$) has been included in the rate expressions, explained in kinetic model part. Also, the non-competitive adsorption of hydrogen with cinnamaldehyde and intermediates was considered in the kinetic model. The solubility model explained earlier was used to predict the k_h [kmol.MPa⁻¹.m⁻³] values. This estimated the solubility values in the reaction mixture depending upon the temperature, cinnamaldehyde concentration in the organic phase and KOH molarity in aqueous phase.

Figure 7: Effect of changing partial pressure of hydrogen on initial rates of hydrogenation at 323 K, 3 M KOH in aqueous phase, 0.3 w/W cinnamaldehyde in organic phase, 12 kg.m⁻³ catalyst loading

Effect of changing KOH molarity in aqueous phase:

As explained earlier, the addition of the aqueous alkali together with the reaction mixture of cinnamaldehyde hydrogenation has shown to increase the selectivity towards cinnamyl alcohol[7,10,12,14,22]. Effect of changing KOH molarity in aqueous phase on overall conversion and selectivity is shown in **Figure 8**. As shown in the graph, there was only 3% conversion and high HCAL selectivity observed when aqueous phase without KOH was used in the reaction mixture. When aqueous phase without KOH was used, the reaction mixture formed an emulsion with water + catalyst dispersed in the organic phase. This entrapment of the catalyst

in the emulsion probably explains the decreased conversion of cinnamaldehyde in this case. The formation of emulsions in two immiscible liquid phases together with solid particles with intermediate hydrophobicity have been explained by Binks et al.[33] in which authors have used toluene-water system with increasing alkalinity of the aqueous phase. With increasing KOH molarity in aqueous phase, the catalyst gets dispersed in the organic phase with clear aqueous phase as reported by Brinks et al.[33] which was also observed in the current study. This explains the increased conversion and COL selectivity steadily up to complete conversion of cinnamaldehyde for increasing KOH molarity from 0-1.2 M. Changing molarity of aq. KOH solution in the range of 1.5 to 3 M did not show any significant effect on conversion and selectivity, 94% conversion with 73% COL selectivity was observed in this range. Further increasing the molarity decreased conversion, while increasing the selectivity towards cinnamyl alcohol. As explained by Binks et al[33] and in the similar study by Henry et al[34] involving separation of mineral particles derived from coal, increasing pH of the aqueous phase made particles more and more hydrophilic with eventual phase inversion. This relation between the physical state of the catalyst and its effects on the conversion and selectivity needs to be investigated more in such GLLS systems.

Figure 8: Effect of changing KOH molarity in aqueous phase on conversion and selectivity at 313 K, 2 MPa, 0.3 w/W cinnamaldehyde in organic phase, 12 kg.m⁻³ catalyst loading

Kinetic Model:

After studying the effects of various operating parameters on the initial rate data, the controlling parameters were identified as initial substrate loading, catalyst loading and partial pressure of hydrogen. The initial rate of hydrogenation for all the species increased proportionally with initial substrate loading, catalyst loading and partial pressure of hydrogen. As explained in the effect of KOH molarity on the rates of hydrogenation, the conversion and selectivity did not change in the range of 1.5 to 3.1 M KOH concentration in the aqueous phase. As this range of KOH concentration is most suitable concerning the conversion and selectivity, most of the parametric studies were performed in this range. In accordance with this, the term for KOH concentration was not included in the rate expressions (eq. 7-10).

The increased selectivity towards cinnamyl alcohol after addition of the fourth liquid phase of aqueous KOH in this GLLS system can be attributed to the hydrogenation of C=C and C=O bonds on different catalytic sites. These two catalytic sites are Pt-only sites and sites affected by KOH i.e. Pt-K⁺ sites. The C=O bond of unsaturated aldehydes get hydrogenated preferentially on the catalytic sites affected by promoter, KOH in this case, as evident from some studies[16,19–21]. In the study by Tronconi et al.[19] regarding hydrogenation of cinnamyl alcohol, the rate of hydrogenation decreased significantly after addition of the promoter Sn. The poisoning of the Pt only sites by addition of the promoter inhibits the further hydrogenation of cinnamyl alcohol to hydrocinnamyl alcohol, thereby increasing its selectivity. This implies that, the C=C bond hydrogenation (hydrogenation of cinnamyl alcohol) is occurring on the catalytic sites which are not affected by the promoter (Pt-only sites). In accordance with this, two different adsorbed states of cinnamaldehyde can be considered, adsorption through C=O bond and its hydrogenation on Pt-K⁺ sites (hydrogenation of cinnamaldehyde and hydrocinnamaldehyde) and adsorption through C=C bond and its hydrogenation on Pt only sites (hydrogenation of cinnamyl alcohol).

Figure 9 below illustrates this discussion,

Figure 9: Cinnamaldehyde hydrogenation scheme showing catalytic sites and preferred route.

$\{[*]_{C=O}$ and $[*]_{C=C}$ - Fractional coverage of Pt-K⁺ and Pt-only sites, respectively on total active catalytic sites}

It is important to consider this two site adsorption mechanism while writing the kinetic model that will adequately explain the advance of cinnamaldehyde hydrogenation in this four phase sytem. To incorporate this, two adsorption coefficients were considered in the model. One adsorption coefficient, K_{CAL} for adsorption through C=O bond i.e. for adsorption of cinnamaldehyde and hydrocinnamaldehyde (although cinnamaldehyde hydrogenation involves hydrogenation of both C=C and C=O bonds, adsorption through C=O bond is favored because of promotion action). Other adsorption coefficient, K_{COL} for adsorption through C=C bond i.e. for adsorption of cinnamyl alcohol (refer **Figure 9**).

The conventional Langmuir-Hinshelwood type of kinetic model[23] was written for each of the two catalytic sites individually (i.e. for adsorption of CAL and HCAL on Pt-K⁺ sites and for

COL adsorption on Pt-only sites) considering the quasi-equilibrated adsorption of all the species getting hydrogenated, non-competitive adsorption of hydrogen on both catalytic sites and irreversible surface reaction as the limiting step. Considering these assumptions, the general rate expression for hydrogenation can be written as-

$$r_i = \frac{k_{0i}K_i[C_i](k_h P_{H_2})w}{1+K_i[C_i]} \quad \text{-----1}$$

Where, r_i [kmol.m⁻³.sec⁻¹] is the rate of reaction by path R_i (**Figure 1**). k_{0i} [m³.kg⁻¹.sec⁻¹] is the actual rate constant for surface reaction by path R_i , K_i [m³.kmol⁻¹] is the adsorption coefficient (K_{CAL} for cinnamaldehyde and hydrocinnamaldehyde and K_{COL} for cinnamyl alcohol).

Both the adsorption isotherms are derived considering the equilibrium between the adsorption and desorption of the species getting hydrogenated (as assumed in Langmuir adsorption isotherms).

$[C_i]$ is the concentration [kmol.m⁻³], k_h is the solubility of hydrogen in reaction mixture [kmol.m⁻³.MPa⁻¹] and P_{H_2} is the partial pressure of hydrogen [MPa], w is catalyst loading, [kg.m⁻³].

In eq. 1, the apparent rate constant k_i [m⁶.kg⁻¹.kmol⁻¹.sec⁻¹] for reaction by path R_i is,

$$k_i = k_{0i}K_i \quad \text{-----2}$$

Writing the mass balance equations for all the species (refer **Figure 1**),

$$\frac{d[CAL]}{dt} = -r_1 - r_2 \quad \text{-----3}$$

$$\frac{d[COL]}{dt} = r_1 - r_4 \quad \text{-----} 4$$

$$\frac{d[HCAL]}{dt} = r_2 - r_3 \quad \text{-----} 5$$

$$\frac{d[HCOL]}{dt} = r_3 + r_4 \quad \text{-----} 6$$

Where,

$$r_1 = \frac{k_{01}K_{CAL}[CAL](k_h P_{H_2})w}{1+K_{CAL}[CAL]} \quad \text{-----} 7$$

$$r_2 = \frac{k_{02}K_{CAL}[CAL](k_h P_{H_2})w}{1+K_{CAL}[CAL]} \quad \text{-----} 8$$

$$r_3 = \frac{k_{03}K_{CAL}[HCAL](k_h P_{H_2})w}{1+K_{CAL}[CAL]} \quad \text{-----} 9$$

$$r_4 = \frac{k_{04}K_{COL}[COL](k_h P_{H_2})w}{1+K_{COL}[COL]} \quad \text{-----} 10$$

Where,

r_1, r_2 are rate expressions for hydrogenation of cinnamaldehyde by reaction path R_1, R_2 , respectively. While r_3, r_4 are the rate expressions for hydrogenation of hydrocinnamaldehyde and cinnamyl alcohol, respectively by reaction path R_3, R_4 as shown in **Figure 1**.

$$K_{CAL} = \frac{k_1}{k_{01}} = \frac{k_2}{k_{02}} = \frac{k_3}{k_{03}} \quad \text{-----} 11$$

$$K_{COL} = \frac{k_4}{k_{04}} \quad \text{-----} 12$$

The thermodynamic model for predicting the hydrogen solubility (k_h values) in the reaction mixture based on the operating temperature, compositions of the organic and inorganic phase (explained earlier) was directly incorporated with this kinetic model.

The *ODE45* solver of the *MATLAB* was used for solving equations 7-10. Using the experimental concentration profiles at different operating conditions, the regression analysis was done using *fminsearch* solver of the *MATLAB* for calculating the kinetic parameters involved.

Figure 10 shows the comparison between experimental batch reaction data and kinetic model results. The operating conditions for the concentration profile shown in **Figure 10** are 313 K, 0.3 w/W of cinnamaldehyde in organic phase, 12 kg/m³ catalyst loading, 2 MPa pressure, 3 M KOH concentration in aqueous phase. As can be seen in **Figure 10**, the L-H model results are in agreement with the experimental concentration profile. It also concludes that, the zero order kinetic model used in the previous study[22] of cinnamaldehyde hydrogenation in similar four phase system cannot satisfactorily explain the intrinsic reaction kinetics.

Figure 10: Comparison between experimental batch reaction data and model results at 313 K, 0.3 w/W of cinnamaldehyde in organic phase, 12 kg/m³ catalyst loading, 2 MPa pressure, 3 M KOH concentration in aqueous phase; [Points- Experimental data, Continuous lines- Model predictions].

While, **Figure 11** shows comparison in terms of conversion and selectivity between experimental data and kinetic model results at 323 K.

Figure 11: Comparison between experimental batch reaction data and model results in terms of conversion and selectivity at 323 K, 0.3 w/W cinnamaldehyde concentration in organic phase, 12 kg/m³ catalyst loading, 2 MPa pressure, 3 M KOH concentration in aqueous phase; [Points- Experimental data, Continuous lines- Model predictions].

The coefficient of determination (R^2) values between model predictions and experimental data, for the graphs of all the species in **Figure 10** and **Figure 11** are more than 0.95.

Table 1 shows the regression results for kinetic parameters involved- rate constants, adsorption coefficients at 313 and 323 K, the activation energies for the individual reactions (R₁-R₄) and free energy of adsorption for adsorption coefficients.

T,K	k_1	k_2	k_3	k_4	K_{CAL}	K_{COL}
313	8.29E-04	2.53E-04	1.99E-03	1.75E-06	5.84E-01	9.29E-04
323	3.35E-03	6.63E-04	3.09E-03	9.41E-05	5.20E+00	1.98E-02
$\Delta E_i, \Delta G_i$ (kJ.mol ⁻¹)	117.46	81.05	36.81	335.07	183.83	257.14

Table 1: Values of rate constants, adsorption coefficients at 313, 323 K and activation energies;

$$k_1, k_2, k_3, k_4 - [\text{m}^6.\text{kg}^{-1}.\text{kmol}^{-1}.\text{sec}^{-1}] ; K_{CAL}, K_{COL} - [\text{m}^3.\text{kmol}^{-1}]$$

ΔE_i in **Table 1** represents the activation energy for respective reaction paths and ΔG_i represents the free energy of the adsorption for K_{CAL} and K_{COL} defined as[35],

$$\Delta G_i = -RT \ln K_i \quad \text{-----13}$$

The values of kinetic parameters reported in **Table 1** are average of the values determined after fitting the experimental data at different operating conditions, maximum 5% error was observed in these values.

T,K	k_1	k_2	k_3	k_4
k_1	1			
k_2	3.28	1		
k_3	0.42	0.12	1	
k_4	473.71	144.57	1137.14	1

Table 2: Correlation matrix for the rate constants at 313 K

Table 2 shows the correlation matrix for the rate constants at 313 K. As shown in **Table 2** the ratio of k_1/k_2 is 3.28, implying the C=O bond hydrogenation is preferred over C=C in cinnamaldehyde in the presence of KOH. Suggesting that the K^+ ions in the vicinity of the catalyst interact with oxygen in the C=O bond leading to its adsorption through C=O. The ratio of k_3/k_4 is 1137.14 indicating the inhibition of the further hydrogenation of cinnamyl alcohol increasing its selectivity in presence of K^+ , while hydrocinnamaldehyde is readily hydrogenated to hydrocinnamyl alcohol. The strong adsorption of the cinnamyl alcohol on the catalyst surface can also be the reason for its inhibition to further hydrogenation[19]. These results show good agreement with the assumptions made in two site adsorption mechanism.

Figure 12: Comparison between experimental batch reaction data by Garkhedkar et al.[14] and model results in terms of conversion and selectivity after 1 hour changing with temperature; [Points- Experimental data, Continuous lines- Model predictions].

Figure 12 shows the temperature dependence of conversion and selectivity at 1 hour after start of reaction for 0.3 w/W cinnamaldehyde concentration in organic phase, 2 MPa pressure, 6 kg.m⁻³ catalyst loading and 3 M aq. KOH solution. Garkhedkar et al.[14] have studied the dependence of rates of cinnamaldehyde hydrogenation in a similar four phase system, the experimental results from Garkhedkar et al.[14] have been compared with the model results from this study in **Figure 12**.

The approach presented in this work will be helpful for understanding kinetics of similar four phase hydrogenation systems. The intrinsic kinetics determined will be incorporated with mixing models for evaluating performance of multiphase flow reactors[36].

Conclusion:

The kinetics of cinnamaldehyde hydrogenation in gas-liquid-liquid-solid four phase system has been determined. The presence of the aqueous alkali greatly shifts selectivity towards cinnamyl alcohol. The initial substrate concentration, catalyst loading, partial pressure of hydrogen are main controlling parameters in cinnamaldehyde hydrogenation in this system. Although the presence of aqueous alkali shifts selectivity towards cinnamyl alcohol, the change in concentration of alkali in aqueous phase does not affect the conversion and selectivity in the range studied in this work. The changes in adsorption mechanism by addition of promoters like aqueous KOH has been discussed by providing two site kinetic approach for cinnamaldehyde hydrogenation on platinum catalyst. By using Langmuir-Hinshelwood kinetic model correlation has been developed between controlling parameters and initial rate of hydrogenation. This correlation seemed to adequately predict the advance of cinnamaldehyde hydrogenation in this system.

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Notation

GLLS System- Gas-Liquid-Liquid-Solid, four phase system

CAL- Cinnamaldehyde

COL- Cinnamyl alcohol

HCAL-Hydrocinnamaldehyde

HCOL- Hydrocinnamyl alcohol

R_1, R_2, R_3, R_4 - Reaction paths 1-4 respectively (**Figure 1**)

r_1, r_2, r_3, r_4 - Rate of reaction for R_1, R_2, R_3, R_4 respectively [$\text{kmol.m}^{-3}.\text{sec}^{-1}$]

$k_{01}, k_{02}, k_{03}, k_{04}$ - Actual rate constants for reactions R_1, R_2, R_3, R_4 [$\text{m}^3.\text{kg}^{-1}.\text{sec}^{-1}$]

k_1, k_2, k_3, k_4 - Apparent rate constants for reactions R_1, R_2, R_3, R_4 [$\text{m}^6.\text{kg}^{-1}.\text{kmol}^{-1}.\text{sec}^{-1}$]

K_{CAL} - Adsorption coefficients for cinnamaldehyde and hydrocinnamaldehyde [$\text{m}^3.\text{kmol}^{-1}$]

K_{COL} - Adsorption coefficients for cinnamyl alcohol [$\text{m}^3.\text{kmol}^{-1}$]

k_h - Henry’s constant, solubility of hydrogen [$\text{kmol.m}^{-3}.\text{MPa}^{-1}$]

P_{H_2} - Partial pressure of hydrogen in [MPa]

w - Catalyst loading [kg.m^{-3}]

T- Temperature [K]

ΔE - Activation Energy [$\text{kJ}\cdot\text{mol}^{-1}$]

ΔG - Free energy of adsorption [$\text{kJ}\cdot\text{mol}^{-1}$]

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