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Kinetics of hydroformylation of 1-decene using carbon-supported ossified HRh(CO)(TPPTS)₃ catalyst

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Funding information

Council of Scientific and Industrial Research (CSIR), India, Grant/Award Number: Task Force on Catalysis and Catalysts (CMM0005.3)

Abstract

The kinetics of hydroformylation of 1-decene has been investigated using a carbonsupported ossified HRh(CO)(TPPTS)₃/Ba catalyst in a temperature range of 343-363 K. The effect of concentration of 1-decene, catalyst loading, partial pressure of H₂ and CO, and stirring speed on the reaction rate has been investigated. A first-order dependence was observed for catalyst concentration and hydrogen partial pressure. The rate showed a typical case of substrate inhibition for high 1-decene concentration. The rate varied with a linear dependence on $P_{\rm CO}$ up to a CO partial pressure of 5-6 MPa in contrast to the general trends; for most of the rhodium-phosphine catalyzed hydroformylation reactions, severe inhibition of rate is observed with an increase in CO pressure. A rate equation has been proposed, which was found to be in good agreement with the observed rate data within the limit of experimental errors. The kinetic parameters and activation energy values have been reported.

KEYWORDS

1-decene, hydroformylation, kinetics, ossification, supported ossified

1 | INTRODUCTION

Homogeneous catalysis, using soluble metal complexes, provides selective synthetic routes under mild operating conditions for many valuable chemicals from simple organic precursors.¹ Homogenous catalytic systems, however, have intrinsic problems related to catalyst-product separation and hence have limited industrial applications. Heterogenization of metal complexes may provide a significant improvement in this aspect. Different approaches, broadly classified as "biphasic catalysis"²⁻⁵ and "solid-supported catalyst".⁶⁻¹¹ The prime requirement for these catalysts is the stability of the complex in the heterogenized phase, which ensures that it does not leach into the noncatalyst liquid phase during the course of a reaction, while retaining the high activity, selectivity, and original configuration of the catalytic complex. Various attempts were made to heterogenize some of the industrially relevant homogeneous catalysts for application to different catalytic reactions including hydroformylation. Although the techniques for heterogenization onto solid supports viz anchored catalyst,⁶⁻¹¹ polymerbound catalyst, ^{12–16} encapsulated catalyst, ^{17–19} supported liquid phase catalyst, (SLPC)²⁰⁻²² supported aqueous phase catalyst (SAPC),^{23,24} supported ionic liquid phase catalyst (SILP),²⁵⁻²⁷ biphasic catalysts using water-soluble metal complexes of sulfonated,²⁻⁵ or fluorinated phosphines²⁸⁻³⁰ ligands, gave active catalysts; they were plagued with problems like leaching and deactivation of the catalysts. Although these concepts have drawn interest, with the exception of aqueous-biphasic catalysis no other approach has been found to be commercially attractive, due to issues of catalyst leaching, catalyst product separation, and poor activity. Even application of aqueous biphasic catalysis is also restricted to

Nomenclature: A, Concentration of H₂ in toluene in equilibrium with gas phase, kmol/m³; B, Concentration of CO in toluene in equilibrium with gas phase, kmol/m³; C, Concentration of the catalyst, kmol/m³; D, Concentration of the 1-decene, kmol/m³; k_1 , Reaction rate constant, $m^{9}/kmol^{3}/s$; K_{2} , Constant in Equation 3, $m^{3}/kmol$; K_{3} , Constant in Equation 3, m³/kmol; P_{CO} , Partial pressure of carbon monoxide, MPa; P_{H_2} , Partial pressure of hydrogen, MPa; r, Rate of hydroformylation, kmol/m³/s; R'_{Ai} , Experimental rates; R_{Ai} , Predicted rates; t, Reaction time, min

the hydroformylation of propylene and butene due to lower solubilities of higher olefins.^{31–33} Heterogenization by "ossification" has recently been proposed, wherein the immobilization of water-soluble Rh and Pd/TPPTS complexes has been achieved by precipitating it as an insoluble salt of Group 2 metals such as Ca, Sr, or Ba.^{34–36} Supported ossified catalysts have been found to be active for the hydroformylation of higher olefins and provide one of the most active and stable heterogenized complex catalyst.³⁵ An investigation into the kinetics of higher olefin hydroformylation would be thus more relevant using such supported ossified catalyst.

There are very few kinetic studies on hydroformylation using solid-supported catalysts.³⁷⁻⁴⁷ The kinetics of hydroformylation of propylene,^{37,38} allyl alcohol,³⁹ and 1-butene⁴⁰ using SLPC, HRh(CO)(PPh₃)₃ was reported by Scholten and co-workers. They have proposed the power law model based on the observed trends. The kinetics of hydroformylation of 1-octene,^{41,42} linalool,⁴³ and long-chain alkene⁴⁴ was studied using SAPC. The trends reported were similar to those observed in the homogeneous media except for the inhibition observed at a higher olefin concentration. Similar observations were reported for the kinetics of hydroformylation of 1-hexene using the Rh/TPPTS complex exchanged on anion exchange resin.⁴⁵ Kinetics of hydroformylation of 1-hexene using HRh(CO)(PPh₃)₃ encapsulated hexagonal mesoporous silica⁴⁶ and gas-phase propene hydroformylation over a SILP rhodium catalyst also have shown similar trends.⁴⁷

We report here a study on the kinetics of hydroformylation using carbon-supported ossified catalyst. Such study will also provide an understanding of the mechanism of the reaction using ossified catalyst and the variation from the reported mechanism using conventional homogeneous HRh(CO)(PPh₃)₃ and HRh(CO)(TPPTS)₃ catalysts.

2 | EXPERIMENTAL

2.1 | Materials

Rhodium trichloride (RhCl₃·3H₂O), obtained from Arora-Matthey (Kolkata, India), was used as received without further purification. 1-Decene (>99% pure) was obtained from Aldrich (St. Louis, MO, USA). Barium nitrate and PPh₃ were procured from Loba Chemie (Mumbai, India). Freshly distilled toluene was used as the solvent. Hydrogen and carbon monoxide (>99.8%) were obtained from Indian Oxygen (Mumbai, India) and Matheson Gas (Montgomeryville, PA, USA), respectively, and used as received. The syngas mixture (H₂ + CO) in the desired ratio, typically 1:1 CO:H₂, was made as a premix from H₂ and CO and stored in a reservoir. The ligand triphenylphosphine trisulfonate (TPPTS)⁴⁸ and its rhodium complex, HRh(CO)(TPPTS)₃, were prepared by following known literature procedures.²³

2.2 | Preparation of supported ossified catalyst

The supported ossified catalyst was synthesized from the water-soluble metal complex $HRh(CO)(TPPTS)_3$ by precipitation as its barium salt on a porous support. In a general synthetic procedure, 20% aqueous $Ba(NO_3)_2$ (2 g, 8.51 mmol) was combined with 10 g of support and refluxed for 4–5 h. The mixture was subsequently dried, resulting in a barium nitrate impregnated support.

1.5 grams of the above-prepared Ba(NO₃)₂ impregnated support (carbon) was taken and added to an aqueous solution of HRh(CO)(TPPTS)₃ (131.5 mg, 0.07 mmol) and TPPTS (240.5 mg, 0.42 mmol, (Rh:P = 1:6)) under argon flow. After 4–5 h of stirring at ~40°C, the mixture was filtered and washed two to three times with cold and hot water, respectively. The solid was further washed in a soxhlet apparatus for 12 h with water and toluene, respectively. This ensured that all unreacted complex was removed. The catalyst was then dried under vacuum (yield = 1.73 g).

2.3 | Experimental setup

All the hydroformylation experiments were carried out in a 50-mL autoclave, supplied by Amar Engineers (India) and was provided with arrangements for liquid and gas sampling, automated temperature control, and a variable stirring speed. The reactor was provided with a rupture disk as a safety measure. The maximum reactor operating pressure and temperature were 2000 psi and 250°C. The reduction of pressure in the syngas reservoir in the course of the reaction was monitored using a pressure transducer/recorder. Figure 1 shows a schematic of the experimental setup.

2.4 | Experimental procedure

In a typical experiment, the desired amounts of the catalyst, olefin, and solvent were charged into the autoclave, and the autoclave was closed. It was then flushed with nitrogen followed by flushing with $CO + H_2$ and heated up to the requisite temperature. Subsequently, syngas with the requisite H_2 and Co ratio was filled in the reactor up to the reaction pressure. A liquid sample was taken as the initial sample of the reactor contents. The reaction was initiated by increasing the stirring speed to the desired value. The syngas premix in a $1:1 \text{ CO:H}_2$ ratio was fed continuously into the reactor to make up for the gas consumption, which was intrinsically in a 1:1 ratio. This was possible because the only products formed was aldehyde (n: iso). This ensured that the ratio of CO: H_2 in the reactor was maintained, as present at the beginning of the reaction. Analysis of the reaction products at the end of the reaction also showed only aldehyde products. Since these reactions were intended to understand the intrinsic kinetics, the reactions times were short so that the liquid phase composition did not vary much, and the data would represent the initial



FIGURE 1 A schematic of the reactor setup used for the hydroformylation reaction

reaction rate and ensure differential conditions. Analysis of the liquid-phase composition for the initial and final samples was conducted to ensure material balance, which was found to be excellent. The rates of the hydroformylation reaction observed in thus initial range were constant with a reproducibility of 5-7%. This procedure was employed to study the influence of the various reaction parameters on the rate of hydroformylation, to assess the activity of the supported ossified catalysts for hydroformylation of 1-decene, and further to study the kinetics of the reaction using carbon-supported ossified catalyst.

2.5 | Analytical methods

The reactants and products were analyzed quantitatively on GC (HP 6890) over an HP-5 column (5% diphenyl and 95% dimethylpolysiloxane stationary phase, 30 M × 320 μ m × 0.25 μ m) An external standard method was used for this purpose.. Calibration of the analysis was done using authentic standards.

3 | RESULTS AND DISCUSSION

The stoichiometric reaction for 1-decene hydroformylation is given in Scheme 1. A few experiments were conducted for a high conversion of 1-decene to confirm the mass balance and reproducibility of experiments. In these experiments, the reactants consumed (1-decene, CO, and H_2) and the products formed (undecanal, iso- C_{11} aldehyde) were compared. A typical concentration time profile is shown in Figure 2. The results showed a good agreement between the reactant consumption and products formed; the results also confirmed that the only products formed were the C_{11} aldehydes. Based on these studies, the rate of aldehyde formation could be represented by monitoring the consumption of syngas with time.

3.1 | Solubility data

The solubility of CO and H_2 in toluene was obtained experimentally as per the reported procedure,⁴⁹ and Henry's constants for H_2 and CO in toluene are presented in Table 1. These values were used to calculate the concentrations of dissolved CO and H_2 in the toluene medium.

Table 2 lists the range of conditions studied for understanding the kinetics of 1-decene hydroformylation using the carbon-supported ossified catalyst. As shown in Figure 3, the initial rates of reaction were calculated from the gas consumption data with respect to time. An initial induction period was observed. This was found to vary with the temperature and was 10, 20, and 30 min for the temperature of 363, 353, and 343 K, respectively. The initial rates of reaction were

$$CH_{3} - (CH_{2})_{7} - CH_{2} - CH_{$$



FIGURE 2 Concentration–time profile for hydroformylation of 1-decene. Reaction conditions: catalyst, 3.7 kg/m³ (0.37 w/w % Rh); 1-decene, 0.39 kmol/m³; *T*, 353 K; stirring speed, 20 Hz; P_{CO+H_2} (1:1), 4.14 MPa; total charge, 2.7×10^{-5} m³; solvent: toluene, time, 6.2 h

TABLE 1 Henry's constants for H₂ and CO in toluene

Sr. no	<i>T</i> (K)	CO (m ³ MPa/kmol)	H ₂ (m ³ MPa/kmol)
1	343	11.70	28.10
2	353	11.53	26.80
3	363	11.24	25.73

TABLE 2 Range of conditions used for the kinetic studies

Catalyst loading (kg/m3) 0.37 wt/wt % Rh	1.85-7.4
Concentration of 1-decene (kmol/m ³)	0.098-0.78
Partial pressure of hydrogen (MPa)	0.68-5.41
Partial pressure of carbon monoxide (MPa)	0.34–9.65
Temperature (K)	343-363
Solvent	Toluene
Stirring speed (Hz)	16.6 - 24.1
Reaction volume (m ³)	2.7×10^{-5}

calculated after correction for the induction period, as per the Equation 1:

$$R = \frac{\text{Slope of product formation vs. time plot}}{\text{Volume of liquid}}$$
(1)

The influence of the different parameters on the initial rate of hydroformylation and the development of the kinetic model are discussed in the following sections.

3.2 | Mass transfer effects

The hydroformylation of 1-decene using the carbonsupported ossified catalyst is a typical case of a three-phase



FIGURE 3 A plot of product formation versus time for different catalyst concentrations. Reaction conditions: 1-decene 0.39 kmol/m³; *T*, 353 K; stirring speed, 20 Hz; $P_{\rm CO-H_2}$ (1:1), 4.14 MPa; total charge, 2.7×10^{-5} m³; solvent, toluene; time, 1 h

TABLE 3 Mass transfer parameters

Sr. no.	Parameter	Criteria	Value range
1	Gas–liquid mass transfer resistance (α_{gl})	< 0.1	6.85×10^{-4} to 1.96×10^{-3}
2	Liquid–solid mass transfer resistance (α_{ls})	< 0.1	2.85×10^{-4} to 9.97 × 10 ⁻⁵
3	Intraparticle diffusion (φ)	< 0.2	8.2×10^{-3} to 1. 62 × 10 ⁻³

(gas–liquid–solid, G-L-S) catalytic reaction, and hence it is essential to check the various mass transfer effects in such systems. The significance of gas–liquid mass transfer resistance (α_{gl}), liquid–solid mass transfer resistance (α_{ls}), and intraparticle diffusion (φ) was analyzed by comparing the rate of reaction, R_i (kmol/m³/s), and the maximum possible rate as per the criteria laid out by Ramachandran and Chaudhari.⁵⁰ The values for various mass transfer parameters are presented in Table 3, which indicate that the reaction operates in the kinetic regime.

3.3 | Effect of stirring speed

The effect of stirring speed on the rate of reaction was studied to further confirm that the reaction operates in the kinetic regime and did not under a mass transfer-controlled condition, As seen in Figure 4, the rate of reaction was independent of the stirring speed beyond, 1000 rpm (16.6 Hz), which clearly indicates that the reaction occurs in the kinetic regime. Therefore, a stirring speed of 1200 rpm (20 Hz) was used for all the studies. This ensured that the data obtained were in the kinetic regime.



FIGURE 4 A plot of rate of hydroformylation of 1-decene versus stirring speed. Reaction conditions: catalyst, 3.7 kg/m³ (0.37 w/w % Rh); 1-decene, 0.39 kmol/m³; *T*, 363 K; $P_{\rm CO+H_2}$ (1:1), 4.14 MPa; total charge, 2.7×10^{-5} m³; solvent, toluene; time, 1 h



FIGURE 5 A plot of rate versus catalyst loading in hydroformylation of 1-decene. Reaction conditions: 1-decene, 0.39 kmol/m^3 ; *T*, 343–363 K; stirring speed, 20 Hz; $P_{\text{CO+H}_2}$ (1:1), 4.14 MPa; total charge, $2.7 \times 10^{-5} \text{ m}^3$; solvent, toluene; time, 1 h

3.4 | Effect of catalyst loading

The effect of catalyst loading on the rate of hydroformylation of 1-decene was studied in the temperature range of 343– 363 K, 1-decene concentration of 0.39 kmol/m³, and a total pressure of CO + H₂ = 4.14 MPa (CO/H₂ = 1). The results are shown in Figure 5. The rate was found to be linearly dependent on the catalyst concentration, indicating a first-order kinetics. An increase in the concentration of catalyst will cause an increase in the effective active catalyst concentration as seen from the reported mechanism in Figure 6, thereby increasing the rate of reaction and hence a first-order dependence is observed.⁵¹

3.5 | Effect of the 1-decene concentration

Figure 7 shows the effect of 1-decene concentration on the rate of hydroformylation in the temperature range of 343–363 K. The plot of rate versus 1-decene concentration passes through the maxima. The rate was found to have a linear dependence on 1-decene in the initial concentration range. At higher substrate concentration, typical substrate inhibited kinetics was observed. This could be due to the formation of diolefinic species in equilibrium, which can reduce the concentration has been reported in kinetics of hydroformylation of olefins using heterogeneous,^{41,42} homogeneous,^{52,53} and biphasic⁵⁴ catalysts.

3.6 | Effect of partial pressure of hydrogen

As seen in Figure 8, the rate of reaction was found to show a first-order dependence on $P_{\rm H_2}$ at a constant CO partial pressure of 2.06 MPa. As per the hydroformylation mechanism (Figure 6), the oxidative addition of H₂ is the rate-determining step. Hence, with increasing pressure of hydrogen the rate enhancement is observed.

3.7 | Effect of partial pressure of carbon monoxide

Figure 9 shows the effect of $P_{\rm CO}$ on the rate of hydroformylation of 1-decene at a 2.07 MPa H₂ partial pressure. A plot of rate versus CO partial pressure passes through maximum. In the initial pressure range, the rate was found to be first order with respect to $P_{\rm CO}$ and inversely dependent on $P_{\rm CO}$ at higher CO pressures. As per the mechanism of rhodium-catalyzed hydroformylation, using triphenyl phosphine trisulfonate ligand (Figure 6), the inhibition with CO occurs due to the formation of inactive di and tricarbonyl acyl rhodium species such as [RCH₂CH₂CORh(CO)₂(TPPTS)₂] and[RCH2CH2CORh(CO)3(TPPTS)]. In general, the inhibition with P_{CO} is observed in the range of 0.3–0.5 MPa.^{55–57} In the case of the supported ossified catalysts, the inhibition is observed at relatively higher P_{CO} , which could be due to the presence of excess TPPTSBa_{3/2} ligand on the support. This makes the phosphine easily available for binding the metal center and prevents the formation of inactive dicarbonyl and tricarbonyl species at lower CO pressures. It is well known that in case of phosphine-modified rhodium systems the maximum rate with P_{CO} is highly dependent upon the Rh: PPh₃ ratio. At a higher ratio, the maximum is observed at higher



FIGURE 6 Mechanism for hydroformylation using HRhCO(TPPTS)₃ catalyst

 $P_{\rm CO}$.⁵⁸ The Rh:P ratio used in this work is 1:6, and hence such an observation is likely.

The role of carbon support on adsorption of H_2 and CO gases may also contribute to the observed trend. It was observed experimentally that the solubility of both the gases is slightly higher in the presence of carbon-supported ossified catalyst (may be due to adsorption of gases on carbon) as compared to the solubility in a solvent alone. Because of the higher availability of the H_2 on the catalyst surface, the formation of inhibiting species may take place at a higher P_{CO} . The inhibition is more pronounced at 363 K, whereas it is barely observed at the lower temperature of 343 K. This observation is in contrast to the trends reported in homogeneous rhodium-

catalyzed hydroformylation, using a triphenyl phosphine ligand, where inhibition with CO occurs at a much lower pressure range.^{59–62}

During the course of this study, it was also observed that the n/i ratio was not strongly influenced by the concentration of the parameter studied. The n/i ratio varied in the range of 2.4–3.0 for all the parameters investigated.

3.8 | Kinetic models

An empirical approach was employed for developing the kinetic rate equation. The independence of the rate on stirring speed and also the analysis of the different mass transfer



FIGURE 7 A plot of rate versus 1-decene concentration effect in the hydroformylation of 1-decene. Reaction conditions: catalyst, 3.7 kg/m³ (0.37 w/w % Rh); *T*, 343–363 K; stirring speed, 20 Hz; $P_{\rm CO+H_2}$ (1:1), 4.14 MPa; total charge, 2.7×10^{-5} m³; solvent, toluene; time: 1 h



FIGURE 8 A plot of rate versus $P_{\rm H_2}$ for the hydroformylation of 1-decene. Reaction conditions: catalyst, 3.7 kg/m³ (0.37 w/w [%] Rh); 1-decene, 0.39 kmol/m³; *T*, 343–363 K; stirring speed, 20 Hz; $P_{\rm CO}$, 2.07 MPa; total charge, 2.7×10^{-5} m³; solvent, toluene; time: 1 h

resistances (Table 3) indicated that the data were indeed representing the true chemical reaction, free of any mass transfer resistances. The initial rate data could thus be used to evaluate the intrinsic kinetic parameters.

Several rate equations based on the observed rate dependencies were proposed as shown in Table 4. A nonlinear regression analysis (Marquardt method) was used to fit the data, and the different kinetic parameters were evaluated. The



FIGURE 9 A plot of rate versus $P_{\rm CO}$ for the hydroformylation of 1-decene. Reaction conditions: catalyst, 3.7 kg/m³ (0.37 w/w [%] Rh); 1-decene, 0.39 kmol/m³; *T*, 343–363 K; stirring speed, 20 Hz; $P_{\rm H_2}$: 2.07 MPa; total charge, 2.7 × 10⁻⁵ m³; solvent: toluene; time, 1

best fit was based on the least minimum error between the predicted and experimental rates as shown in Equation 2:

$$\Phi = \sum_{i=1}^{n} \left[R_{Ai} - R'_{Ai} \right]^2$$
(2)

where Φ , which represents the sum of the squares of the difference between the observed and predicted rates, is the objective function to be minimized (Φ_{\min}); *n* is the number of experimental data, whereas R_{Ai} and R'_{Ai} are the predicted and experimental rates, respectively. Table 4 also shows the values of the rate parameters and Φ_{\min} .

The following criteria were used to discriminate the rate models: (i) thermodynamic viability, (ii) activation energy values, and (iii) the error (Φ_{min}) between the experimental and predicted rates, i.e. the fitting of the equation. Rate models II and III showed inconsistency of the equilibrium constants and also had high activation energy and were not considered further. Since negative values of rate parameters were not possible, Model V was rejected. The Φ_{min} value for model IV was higher than that for model I. Hence, model I (Equation 3) was considered the best model to represent the kinetics of hydroformylation of 1-decene in the presence of a carbon-supported ossified catalyst:

$$r = \frac{k_1 A B C D}{(1 + K_2 D)^2 (1 + K_3 B)^2}$$
(3)

In this equation, k is the intrinsic rate constant $(m^9/kmol^3/s)$, whereas the different concentrations are represented as follows:

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TABLE 4	Values of kinetic parameters at	different tempe	ratures			
Model	Rate model	T (K)	k ₁	Ka	K ₂	φ
I	$r = \frac{k_1 A B C D}{(1 + K_2 D)^2 (1 + K_2 B)^2}$	343	3.14×10^{-3}	3.95	9.58×10^{-1}	8.76×10^{-12}
	(11122) (11132)	353	5.92×10^{-3}	4.97	9.46×10^{-1}	3.60×10^{-11}
		363	1.16×10^{-2}	5.90	9.24×10^{-1}	1.54×10^{-10}
Π	$r = \frac{k_1 A B C D}{(1 + K_2 D^2)(1 + K_3 B^2)}$	343	1.43×10^{-3}	1.76×10^{1}	2.95	8.12×10^{-12}
		353	3.27×10^{4}	4.90×10^{8}	9.17×10^{-4}	1.20×10^{-9}
		363	4.49	3.40×10^4	1.82×10^{-2}	5.24×10^{-9}
III	$r = \frac{k_1 A B C D}{(1+K_2 D)(1+K_3 B)}$	343	1.51×10^{-2}	7.23×10^{1}	2.64	1.13×10^{-11}
	. 2 5 .	353	2.88×10^{-2}	7.35×10^{1}	2.61	4.60×10^{-11}
		363	5.17×10^{-1}	6.95×10^2	2.52	2.06×10^{-10}
IV	$r = \frac{k_1 A B C D}{\left(1 + K_2 D\right)^2 \left(1 + K_3 B\right)}$	343	3.42×10^{-3}	3.98	2.72	9.78×10^{-12}
		353	6.29×10^{-3}	3.93	2.64	4.00×10^{-11}
		363	5.67×10^{2}	3.91	3.65×10^{5}	2.31×10^{-9}
V	$r = \frac{k_1 A B C D}{\left(1 + K_2 D\right)^3 \left(1 + K_3 B\right)^3}$	343	2.52×10^{-3}	1.90	5.84×10^{-1}	9.57×10^{-12}
	<u> </u>	353	1.26×10^{3}	3.82×10^{3}	-1.47×10^{-1}	6.08×10^{-9}
		363	9.42×10^{-3}	1.91	5.62×10^{-1}	1.68×10^{-10}



FIGURE 10 Comparison of experimental rates and rates predicted using model I

A: concentration of H_2 in toluene, kmol/m³, B: concentration of CO in toluene, $kmol/m^3$, C: concentration of catalyst, $kmol/m^3$, and D: 1-decene concentration, $kmol/m^3$.

The rate parameters for Equation 3 for all the temperature are presented in Table 4 (entry 1).

Figure 10 shows good agreement between the experimental and predicted rates, with an average deviation of $\pm 5\%$. The activation energy was evaluated as 67.94 kJ/mol from



FIGURE 11 Temperature dependence of rate constant

the Arrhenius plot shown in Figure 11. The rate parameters K_2 and K_3 show opposite trends. Both K_2 and K_3 are in fact lumped parameters, which describe the overall trends and not individual equilibrium constants. Such a behavior is thus, possible.

The validity of the proposed model I was cross-checked by plotting the experimental and observed rates at varying concentrations of the variables for all temperatures (Figure 12). The model was found to predict the trends in good agreement with experimental observations.



FIGURE 12 Validation of the proposed rate model for various reaction parameters

4 | **CONCLUSIONS**

The ossified HRh(CO)(TPPTS)₃ catalyst supported on carbon was found to be the best considering the stability of the catalyst as compared to that ossified catalyst on other supports. The detailed analysis of the various mass transfer effects in the G–L–S system was evaluated. The kinetics of 1-decene hydroformylation using the carbon-supported ossified catalyst in toluene has been investigated in a temperature range of 343– 363 K. The rate was found to be first order with respect to catalyst and partial pressure of hydrogen. The plots of rate versus 1-decene concentration as well as $P_{\rm CO}$ passed through maxima and show typical substrate inhibition at higher concentrations. In the lower concentration range, the rate was found to be first order with respect to ligand and $P_{\rm CO}$

This kinetics using the carbon-supported ossified catalyst is different from kinetics observed in homogeneous and biphasic catalysis with respect to the substrate concentration effect, which shows the substrate inhibition effect at a higher substrate concentration. An unusual observation for this catalyst is the positive order with respect to $P_{\rm CO}$ up to a pressure of 5–6 MPa. Other parametric effects were found to be similar

to that observed in homogeneous and biphasic media. A rate equation has been proposed based on the observed data, which is in full agreement with the experimental rates obtained. The activation energy was calculated to be 67.94 kJ/mol.

ACKNOWLEDGMENTS

Research fellowship provided by CSIR India to NSP is acknowledged. The funding provided by the Task Force on Catalysis from the CSIR (CMM0005.3) is also acknowledged.

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How to cite this article: Pagar NS, Deshpande RM. Kinetics of hydroformylation of 1-decene using carbon supported ossified HRh(CO)(TPPTS)₃ catalyst. *Int J Chem Kinet*. 2018;1–11. <u>https://doi.org/10.1002/</u> kin.21234