Hydroformylation of 1-hexene using Rh/TPPTS complex exchanged on anion exchange resin: kinetic studies

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Abstract

The exchange of the Rh/Triphenylphosphine trisulfonate sodium [TPPTS] complex on to an anion exchange resin results in a stable heterogenized catalyst for the hydroformylation of alkenes. The kinetics of hydroformylation of 1-hexene using Rh/TPPTS complex exchanged on anion exchange resin to Amberlite IRA-93 has been investigated for the first time. The rate of the reaction was found to be dependent on the partial pressure of hydrogen and 1-hexene concentrations with a first order. A maximum in the rate with increasing partial pressure of carbon monoxide was observed. A rate model has been proposed which predicts the observed rate data within reasonable error. The activation energy was found to be 84.37 kJ/mol.
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Keywords: Hydroformylation; Kinetics; Heterogenized catalyst; Ion-exchange resin; Rhodium

1. Introduction

The hydroformylation reaction is one of the most important industrial processes exclusively relying on homogeneous catalysis. This process produces the aldehydes by interaction of olefins with syngas in the presence of catalysts as shown below.
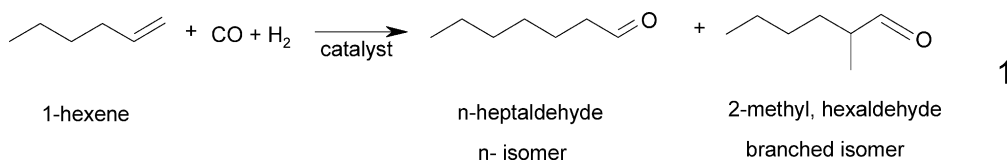
The application of water-soluble catalysts for hydroformylation reaction has been a major development in oxo technology [1]. However, due to problems associated with the solubility of the substrates in aqueous media, the application of this technology in commercial practice has been restricted to propylene and butene hydroformylation [2]. Heterogenization of the precious metal catalysts onto numerous supports has been envisaged, for more productive reactions and effi-

cient catalyst product separation [3]. The binding of the active metal complexes to ion exchange resins has been one such proposition [4]. In this paper, we report on the kinetics of hydroformylation of 1 hexene using Rh/Triphenylphosphine trisulfonate sodium (TPPTS) complex exchanged on to Amberlite IRA-93 Anion exchange resin.

2. Experimental

2.1. Materials

RhCl$_3$ was obtained from Ms Aldrich, CO and H$_2$ were obtained from Specialty Gas Co., India. TPPTS was synthesized from triphenyl phosphine and oleum by a well-documented procedure [5]. The water-soluble catalyst was prepared by ex-

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Nomenclature

D	concentration of 1-hexene (kmol m^{-3})
k	intrinsic rate constant (MPa^{-2} s^{-1})
K_b	constant (MPa^{-1})
K_d	constant (m^3 kmol^{-1})
P_A	partial pressure of hydrogen (MPa)
P_B	partial pressure of carbon monoxide (MPa)
R	rate of hydroformylation reaction (kmol m^{-3} s^{-1})
ϕ_{min}	sum of the squares of the error between the predicted and experimental rates

change method. The anion exchange resin Amberlite IRA-93 used for this purpose was obtained from Fluka, Switzerland.

2.2. Procedure for preparation of the resin catalyst

The Amberlite IRA-93 resin was first wetted with water and washed with 10% HCl. The chloride form of resin was then subsequently converted to the Triphenylphosphine trisulfonate [TPPTS] form by exchange with a 15% solution of the TPPTS sodium salt. The resin was washed thoroughly with distilled water followed by ethanol and then dried.

Prior to the reaction a known quantity of the dry resin in TPPTS form was added to a solution of [Rh(COD)Cl]$_2$ in toluene (known concentration of Rh), under stirring. The rhodium was taken up by the TPPTS by complexation, with a consequent decolorization of the toluene. The analysis of toluene for Rh content showed a Rh concentration of <0.1 ppm, indicating that all the rhodium was complexed with the resin bound TPPTS. This resin was then washed with ethanol, and taken for reaction. The catalyst used for this study had a Rh content of 2.106 mg per g of dry resin.

2.3. Apparatus and procedure for high pressure reactions

The reactions were carried out in a 300 ml high-pressure stainless steel reactor manufactured by Parr Instrument Co., USA. This reactor was fitted with a transducer for monitoring of pressure, a temperature control with automatic heating and cooling, and a magnetic stirrer with variable speed. A reservoir filled with syngas was connected to the reactor via a constant pressure regulator. This enabled continuous feeding of the syngas from the reservoir, as per the consumption in the reactor, while maintaining the pressure in the reactor constant. The reaction was monitored by observing the pressure drop in the reservoir. For the reaction, the reactants and catalyst were charged into the reactor and the reactor was flushed with nitrogen and syngas. Following this the reactor and contents were heated to the desired temperature under low stirring (200 rpm). Once the temperature was attained the

syngas (CO:H$_2$, 1:1) and CO or H$_2$ as required were pressurized into the reactor. The reaction was started by increasing the agitation speed to 1000 rpm. The gas consumed by the reaction was made up by a continuous addition of syngas (CO:H$_2$, 1:1) from the reservoir, wherein the pressure was monitored with time. During the course of the reaction, samples were withdrawn periodically and analysed by GC for reactant and products. For kinetic measurements, the reactions were conducted for fixed time duration, whereas for the screening study the reactions were conducted to high levels of conversion of 1-hexene. At the end of the reaction the autoclave was cooled and final samples were taken for analysis and confirmation of the mass balance.

The analysis of the products and reactants was done using GLC-HP 6890, on a HP-5 capillary column programmed between 33 and 290 °C.

3. Results and discussion

3.1. Preliminary reactions

A few reactions were taken to assess the feasibility of this catalyst for the hydroformylation of hexene-1. The main reactions observed were the formation of the normal and branched aldehydes, along with the isomerisation of hexene. The reactions are presented below.
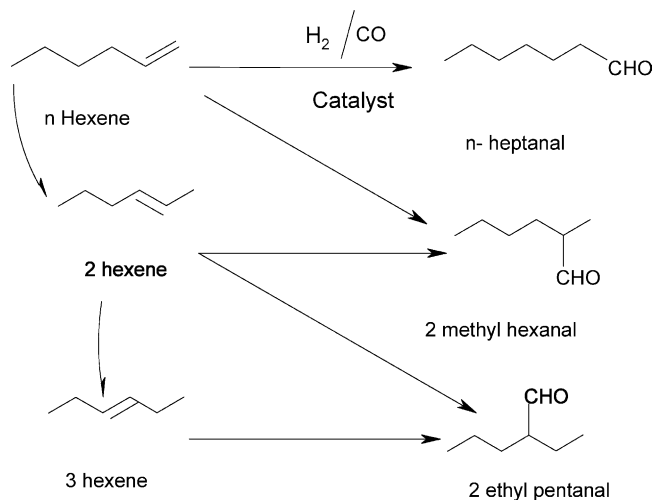
Scheme for hydroformylation of 1-hexene

The analysis of the contents of the reaction indicated that the absorption of the syngas was commensurate with the formation of aldehydes and the consumption of olefins for the hydroformylation products. Since the role of the solvent is extremely important for this reaction from the point of view of selectivity to aldehyde as well as affecting the swelling characteristics of the resin/catalysts numerous solvents were screened to assess their influence on activity and selectivity to the reaction. The results are presented in Table 1.

A major side reaction with this catalyst was the isomerisation reaction, which occurred to the extent of ~58% in

Table 1
Comparison of solvents for hydroformylation reaction

No.	Solvent	1-Hexene conversion (%)	Selectivity to aldehyde (%)	n/iso	Isomerisation (%)
1	Ethanol	79.71	71.40	2.31	19.91
2	Methanol	97.29	62.32	2.26	36.70
3	Acetone	95.91	60.89	2	39.87
4	Water	85.0	48.9	1.6	51.1
5	Toluene	96.76	53.73	1.0	49.20
6	Benzene	99.29	46.98	0.88	53.43
7	Cyclohexane	99.03	42.37	0.88	58.72

Reaction conditions: 1-hexene concentration = 0.42 kmol m^{-3}, P_{CO} = 2.068 MPa, P_{H_2} = 2.068 MPa, catalyst concentration = 5.11 × 10^{-9} kmol Rh g^{-1}, resin = 1 g, reaction temperature = 363 K, rpm = 1000, solvent = 7.5 × 10^{-5} m^{-3}, reaction time = 240 min.

case of cyclohexane solvent. The isomerisation of olefins is reduced in ethanol, accounting for only ~20%. The selectivity to the normal aldehyde was also improved in ethanol solvent as against solvents like cyclohexane, toluene. A concentration–time profile of the reaction is shown in Fig. 1, for ethanol solvent. Since ethanol was observed to be the best solvent for this reaction, all kinetic studies were carried out using ethanol.

One important feature of the reaction performed using the Ion exchange bound catalyst was the near constancy of the n/iso aldehyde ratio. In homogeneous reactions, the n/iso ratio progressively drops with olefin conversion, mainly because the isomerized olefin undergoes hydroformylation leading to exclusively the branched aldehydes [6]. In the current catalytic reaction the n/iso ratio is maintained constant throughout the reaction, this is inspite of the isomerisation of the olefin observed. The results indicate that the reaction

of the isomerized olefins is not facile using the ion exchange bound catalyst. Probably the access of these olefins to the hydroformylation catalyst is hindered, permitting a reaction of only the 1-hexene.

The catalyst was tested for its activity on recycle and leaching. The catalyst was filtered and reused for subsequent reaction. A total of five recycles were conducted without any major variation in activity, selectivity or n/iso ratio. The rhodium was below 0.1 ppm in the reaction medium. The results are shown in Fig. 2.

3.2. Kinetic studies

The kinetics were studied under the following range of conditions, viz. (i) P_{CO}, 0.34–5.52 MPa, (ii) P_{H_2}, 0.69–3.45 MPa, (iii) 1-hexene concentration varying from 0.25 to 1.0 kmol m^{-3} in a temperature range of 353–373 K.

For the kinetic studies, the data were observed for only the initial period wherein the concentration of the olefin changed
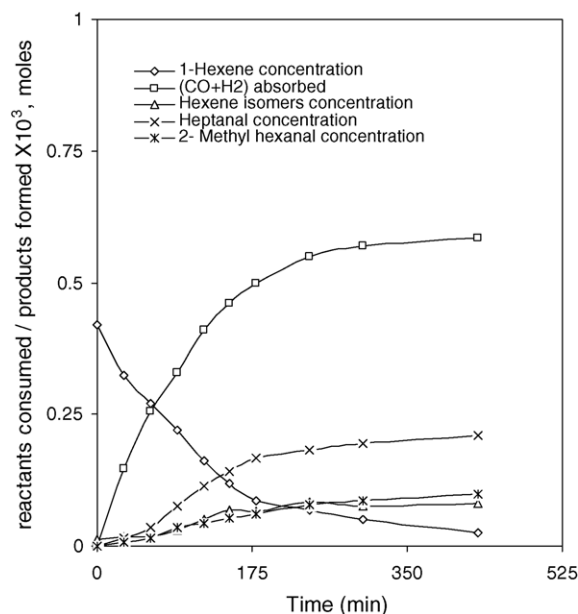

Fig. 1. Concentration time profile of 1-hexene hydroformylation. Reaction conditions: catalyst concentration = 5.11 × 10^{-9} kmol Rh g^{-1}, resin = 1 g, P_{CO} = 2.068 MPa, P_{H_2} = 2.068 MPa, 1-hexene concentration = 0.4998 kmol m^{-3}, rpm = 1000, ethanol = 7.5 × 10^{-5} m^3, reaction temperature = 363 K, reaction time = 430 min.
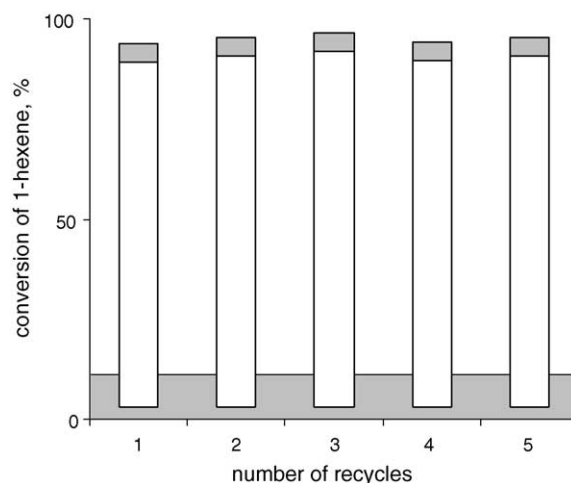

Fig. 2. Catalyst recycle study; reaction conditions: catalyst concentration = 5.11 × 10^{-9} kmol Rh g^{-1}, P_{CO} = 2.068 MPa, P_{H_2} = 2.068 MPa, 1-hexene concentration = 0.4998 kmol m^{-3}, rpm = 1000, ethanol = 7.5 × 10^{-5} m^3, reaction temperature = 363 K, reaction time = 240 min.

marginally ($\sim$10%). The rate was calculated from the concentration time profiles, as the rate of formation of the aldehydes. This methodology ensured that exclusively the rate of hydroformylation was measured. Since the gas consumption was also found to be commensurate with the aldehyde formation, the methodology was assumed to be correct. As another advantage of observing initial data was to avoid acetal formation, observed in ethanol solvent, at higher temperatures and extended reaction times. For kinetic studies, the acetal, where formed, was also taken into consideration while calculating the overall rate of aldehyde formation.

3.3. Effect of 1-hexene concentration

The effect of 1-hexene concentration on the rate of hydroformylation and n/iso aldehyde ratio was studied at a CO and H$_2$ partial pressure of 2.068 MPa each, a catalyst loading of 1 g (5.11×10^{-9} kmol Rh) in ethanol solvent in a temperature range of 353–373 K. The results are presented in Fig. 3.

The rate increases linearly with increasing 1-hexene concentrations in the range studied. The first order behavior with respect to olefin concentration is generally found in hydroformylation reaction [7]. This observation, however, contrasts the observation by Deshpande and Chaudhari [8], wherein a maximum in rate has been observed with 1-hexene in ethanol solvent. A first order behavior is generally expected with olefin in hydroformylation reactions, as the enhanced olefin will increase the formation of alkyl rhodium species (Steps 4 and 10) shown in the hydroformylation mechanism (Fig. 4) [9].

The selectivity to the normal aldehyde was also found to improve with enhanced 1-hexene concentrations, at all the temperatures studied, as shown in Fig. 5. The dependence was more pronounced at higher temperature.
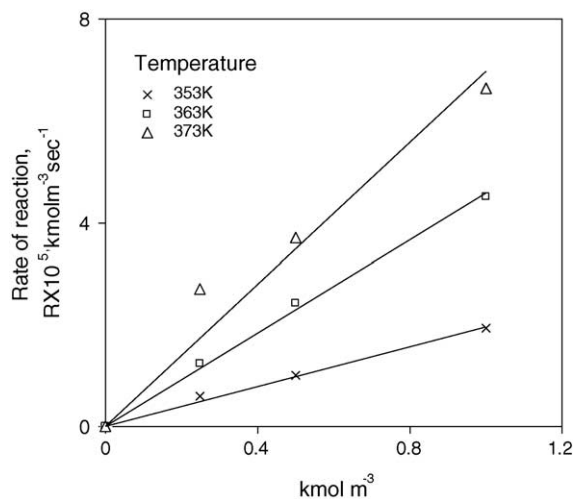

Fig. 3. Effect of olefin concentration on rate of hydroformylation. Reaction conditions: catalyst concentration $= 5.11 \times 10^{-9}$ kmol Rh g^{-1}, resin $= 1$ g, $P_{CO} = 2.068$ MPa, $P_{H_2} = 2.068$ MPa, rpm $= 1000$, ethanol $= 7.5 \times 10^{-5}$ m^3.

3.4. Effect of partial pressure of carbon monoxide

The effect of partial pressure of carbon monoxide on the rate of hydroformylation and n/iso aldehyde ratio was studied at a H$_2$ partial pressure of 2.068 MPa, a catalyst loading of 1 g (5.11×10^{-9} kmol Rh) and a 1-hexene concentration of 0.4998 kmol m^{-3}, in ethanol solvent in a temperature range of 353–373 K. The results are presented in Fig. 6.The rate first increased with increasing P_{CO} and then decreased with further increase in CO partial pressure. The inhibition in rate with enhanced CO pressure is a well-known phenomenon in hydroformylation chemistry. However, the inhibition observed in the case of the ion exchange resin bound catalyst is not as strong as that observed in other homogeneously catalyzed reaction, particularly in ethanolic solvent [8]. The n/iso ratio was also found to be strongly dependent on the partial pressure of CO, particularly at lower temperature. The n/iso ratio dropped with increasing P_{CO}. This effect was less pronounced at higher temperature of 373 K. The results are presented in Fig. 7.

3.5. Effect of partial pressure of hydrogen

The effect of partial pressure of hydrogen on the rate of hydroformylation and n/iso aldehyde ratio was studied at a CO partial pressure of 2.0685 MPa, a catalyst loading of 1 g (5.11×10^{-9} kmol Rh) and a 1-hexene concentration of 0.4998 kmol m^{-3}, in ethanol solvent in a temperature range of 353–373 K. The results are presented in Fig. 8.

The rate was found to be dependent on the hydrogen partial pressure with a first order. Since the oxidative addition of hydrogen to the acyl carbonyl rhodium phosphine species (Step 6, Fig. 4) is the rate-determining step, increase in the partial pressure of hydrogen would lead to increased rates of hydroformylation. The n/iso ratio was found to decrease with increase in hydrogen pressure at all the temperatures studied as seen in Fig. 9.

3.6. Effect of catalyst concentration

The effect of catalyst concentration on the rate of hydroformylation was studied at a CO and H$_2$ partial pressure of 2.068 MPa each, a resin loading of 1 g and a 1-hexene concentration of 0.4889 kmol m^{-3}, in ethanol solvent at a temperature of 363 K. The results are presented in Fig. 10.

For this study, the loading of the resin was kept constant and the rhodium content of the resin was doubled. The rate was found to have a linear dependence on catalyst concentration as expected.

3.7. Rate model

For the purpose of development of rate models, an empirical approach was followed. Prior to discrimination of rate equations, the rate data were analysed for the importance of mass transfer resistances. In the current case, this was more
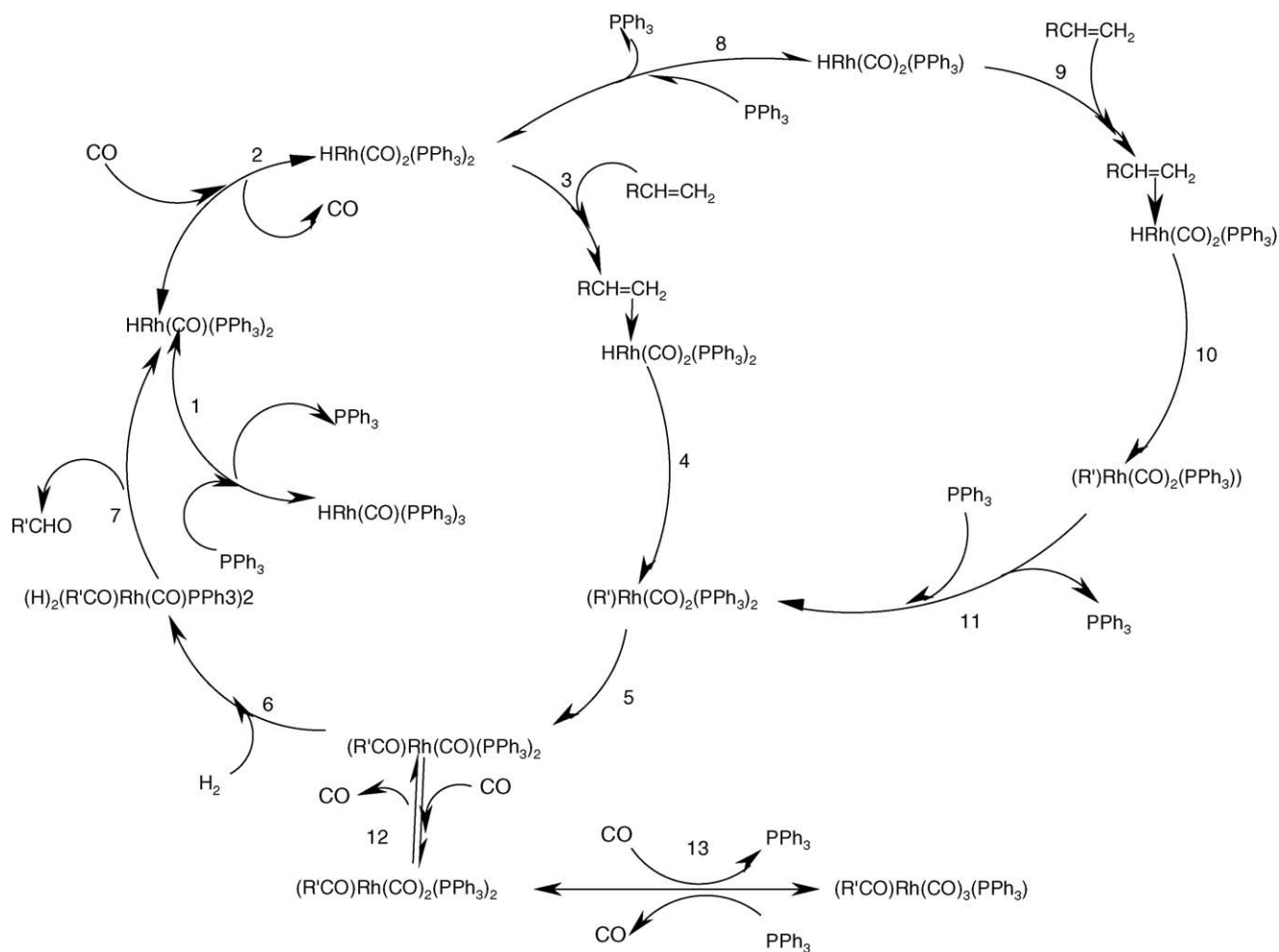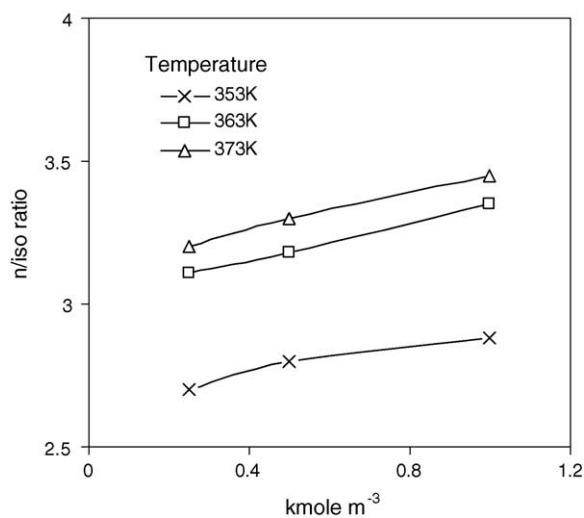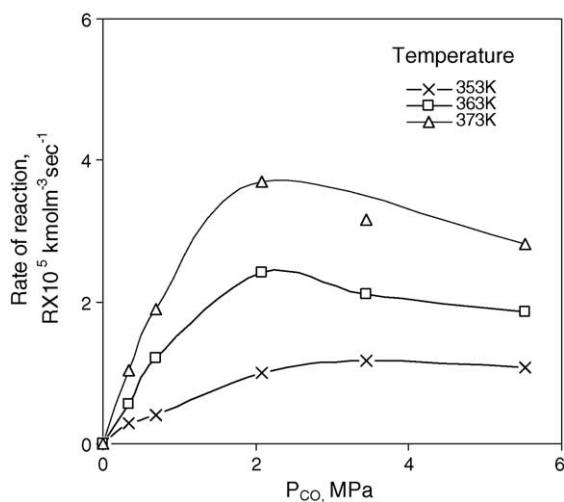
Fig. 4. Mechanism of hydroformylation reaction.

Fig. 5. Effect of olefin concentration on *n/iso* ratio. Reaction conditions: catalyst concentration = 5.11×10^{-9} kmol Rh g^{-1}, resin = 1 g, P_{CO} = 2.068 MPa, P_{H_2} = 2.068 MPa, rpm = 1000, ethanol = 7.5×10^{-5} m^3.

Fig. 6. Effect of P_{CO} on rate of hydroformylation. Reaction conditions: 1-hexene concentration = 0.4998 kmol m^{-3}, catalyst concentration = 5.11×10^{-9} kmol g^{-1}, resin = 1 g, P_{H_2} = 2.068 MPa, rpm = 1000, ethanol = 7.5×10^{-5} m^3.
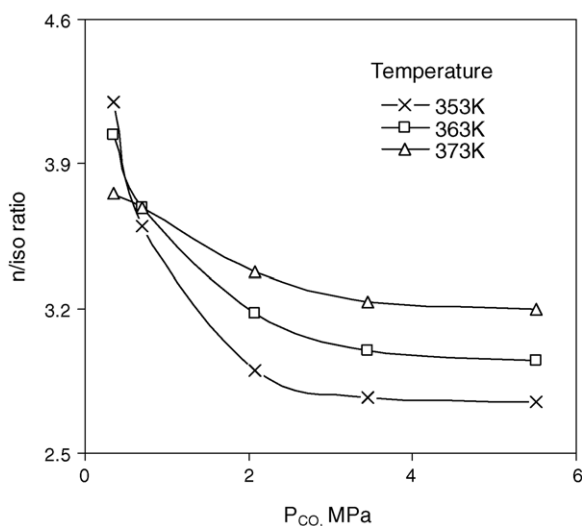
Fig. 7. Effect of P_{CO} on *n/iso* ratio. Reaction conditions: 1-hexene concentration = 0.4998 kmol m^{-3}, catalyst concentration = 5.11 × 10^{-9} kmol g^{-1}, resin = 1 g, P_{H_2} = 2.068 MPa, rpm = 1000, ethanol = 7.5 × 10^{-5} m^3.

Fig. 9. Effect of P_{H_2} on *n/iso* ratio. Reaction conditions: 1-hexene concentration = 0.4998 kmol m^{-3}, P_{CO} = 2.068 MPa, catalyst concentration = 5.11 × 10^{-9} kmol g^{-1}, resin = 1 g, rpm = 1000, ethanol = 7.5 × 10^{-5} m^3.

important since the reaction is a typical gas–liquid–solid reaction. The effect of agitation speed on the rate was investigated at the highest catalyst concentration studied. The rate was found to be independent of the agitation speed, and hence the data were representative of the true kinetics of the reaction. The analysis of the initial rate data according to the criteria laid down by Ramachandran and Chaudhari [10] confirmed that the gas–liquid, liquid–solid and intra-particle mass transfer resistances were negligible. Since the data were found to represent the true kinetics of the reaction, these data were fitted to numerous rate equations similar to the Langmuir Hinshelwood model, considering the trends observed with the different parameters as given in Table 2.
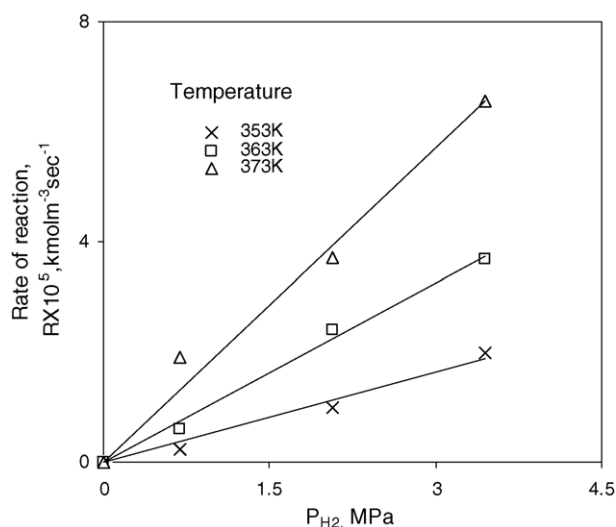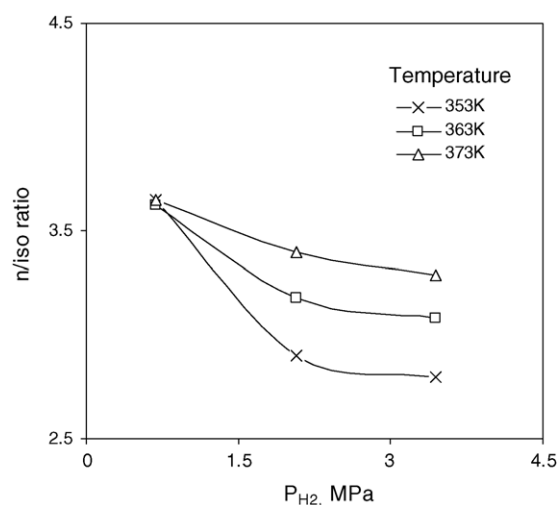
A rigorous discrimination of the rate models was carried out. Based on the ϕ_{min} values for the models and other thermodynamic consideration the model 5 shown below was found to best represent the data observed:

$$R = \frac{k P_A P_B [D]}{1.0 + K_b P_B^2} \qquad (2)$$

This model was best suited for the observed data. Models 1 and 3 did not predict the inhibition in the rate with P_{CO}, whereas models 2 and 4 were not taken into consideration as the ϕ_{min} values were above that for model 5. The plot showing a comparison of the experimental and predicted rates using this model is presented in Fig. 11, which shows a very good fit (average error ±9%). The constants k and K_B were evaluated

Fig. 8. Effect of P_{H_2} on rate of hydroformylation. Reaction conditions: 1-hexene concentration = 0.4998 kmol m^{-3}, catalyst concentration = 5.11 × 10^{-9} kmol g^{-1}, resin = 1 g, P_{CO} = 2.068 MPa, rpm = 1000, ethanol = 7.5 × 10^{-5} m^3.

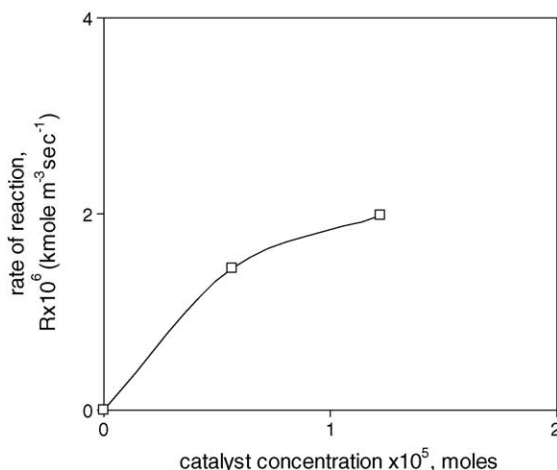Fig. 10. Effect of catalyst concentration on rate of hydroformylation. Reaction conditions: 1-hexene concentration = 0.4998 kmol m^{-3}, P_{CO} = 2.068 MPa, resin = 1 g, P_{H_2} = 2.068 MPa, rpm = 1000, ethanol = 7.5 × 10^{-5} m^3.

Table 2
Rate models evaluated for fitting of data

S. no.	Rate model	T (K)	K ($\times 10^5$ MPa^{-2} s^{-1})	K_b (MPa^{-1})	K_d (m^3 kmol^{-1})	ϕ_{min} ($\times 10^{10}$)
1	$R = \frac{kP_A P_B [D]}{(1.0 + K_b P_B)^2}$	353	0.86	0.221	–	0.469
		363	2.58	0.325	–	1.15
		373	5.29	0.428	–	4.71
2	$R = \frac{kP_A P_B [D]}{(1.0 + K_b P_B)^3}$	353	0.847	0.1538	–	0.953
		363	2.42	0.1943	–	1.96
		373	5.01	0.2117	–	2.44
3	$R = \frac{kP_A P_B [D]}{(1.0 + K_b P_B)^2 (1.0 + K_d D)}$	353	0.765	0.164	0.284	0.891
		363	3.01	0.291	0.516	2.11
		373	6.84	0.296	0.845	3.73
4	$R = \frac{kP_A P_B [D]}{(1.0 + K_b P_B)^3 (1.0 + K_d D)}$	353	0.99	0.1002	0.2797	0.168
		363	2.63	0.1631	0.1314	0.409
		373	5.62	0.1668	0.8328	3.66
5	$R = \frac{kP_A P_B [D]}{1.0 + K_b P_B^2}$	353	0.683	0.091	–	0.127
		363	1.69	0.1498	–	0.199
		373	3.16	0.20	–	2.37

P_A and P_B are the partial pressure of H$_2$ and CO in MPa, respectively; D is the concentration of 1-hexene in kmol m^{-3}.

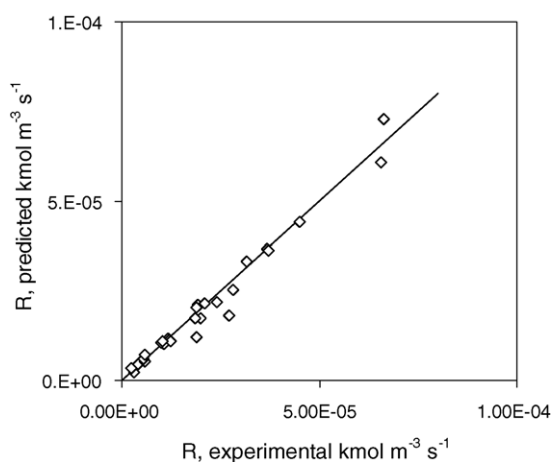
Fig. 11. Comparison of predicted vs. experimental rates.

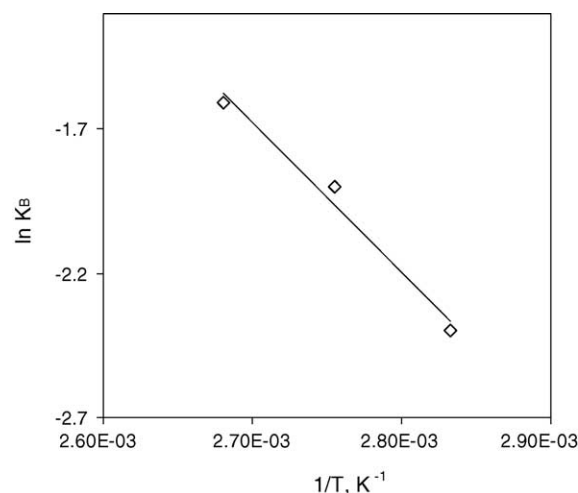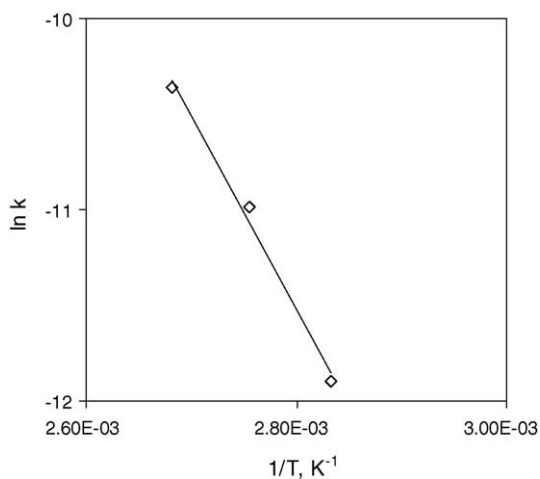
Fig. 13. Plot of ln K_B vs. 1/T.

Fig. 12. Plot of ln k vs. 1/T.

for all the temperatures. An Arrhenius plot of the intrinsic rate constant k (Fig. 12) gave activation energy of 84.37 kJ mol^{-1}.

The constant K_B was found to be dependent on the temperature and increased at higher temperatures as seen in Fig. 13.

4. Conclusions

The kinetics of hydroformylation of 1-hexene using a Rh/I.E. resin bound TPPTS catalyst has been reported for the first time. The rate was found to be first order dependent on catalyst, 1-hexene concentrations and hydrogen partial pressure. The rate was found to pass through a maximum with partial pressure of carbon monoxide and showed a complex dependence. An unusual observation was the near constancy

of the *n/iso* aldehyde ratio with hexene conversion. The results indicate that the hydroformylation of the isomerized hexenes is not favored over this catalyst, which could probably be due to hindered access for these molecules. The catalyst was extremely stable and could be recycled with no loss in activity or selectivity for five recycles. The model which was found to represent the kinetic data was as follows:

$$R = \frac{kP_A P_B [D]}{1.0 + K_b P_B^2}$$

Activation energy of $84.37 \, \text{kJ} \, \text{mol}^{-1}$ was calculated.

Acknowledgement

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