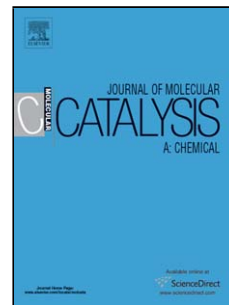


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Graphical Abstract

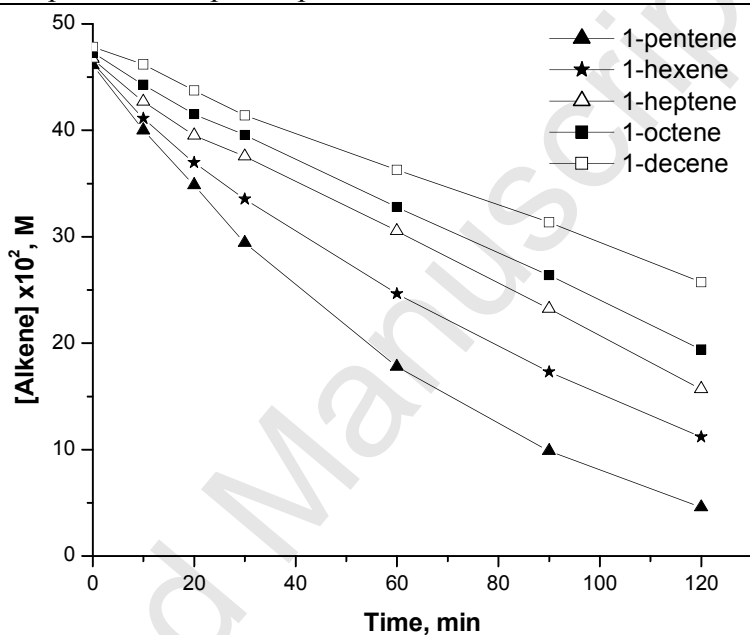
Investigations on the kinetics of hydroformylation of 1-hexene using $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated hexagonal mesoporous silica as a heterogeneous catalyst

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The hydroformylation of linear alkenes by a heterogeneous catalyst system, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated into the pores of HMS acting as nanophase reactor, indicated that the rates were decreased on increasing the chain length. In the kinetics of a representative alkene, 1-hexene the rates were influenced on increasing, 1-hexene concentration, catalyst amount, temperature and partial pressures of CO and H_2 .



Time dependent consumption of alkenes during the reaction at alkene = 47.6×10^{-2} M, catalyst = 100 mg, $p_{\text{CO}} = 20$ bar, $p_{\text{H}_2} = 20$ bar, $T = 80$ °C, Toluene = 50mL

**Investigations on the kinetics of hydroformylation of 1-hexene using
HRh(CO)(PPh₃)₃ encapsulated hexagonal mesoporous silica as a heterogeneous
catalyst**

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Abstract

Kinetics of HRh(CO)(PPh₃)₃ encapsulated in hexagonal mesoporous silica has been investigated for the heterogeneous catalyzed hydroformylation of 1-hexene. The rates of hydroformylation of C₅-C₁₂ alkenes, determined under identical conditions, indicated a decreasing trend on increasing the chain length of the alkenes. The representative alkene, 1-hexene has been subjected for detail kinetic investigations. The 1-hexene hydroformylation kinetics has been studied as the function of the amount of catalyst, concentration of 1-hexene, partial pressure of CO and H₂, and temperature. All these parameters were found to influence the rate of hydroformylation. The rate was observed to be first order with respect to partial pressure of hydrogen. The rate was observed to increase with the increase in the amount of the catalyst and approached saturation on increasing the catalyst amount. Rates increased on increasing the CO pressure and 1-hexene concentration up to certain values, and on further increasing these parameters, substrate inhibited kinetics was observed for both CO and 1-hexene at higher pressures and concentrations respectively. A kinetic rate model based on the mechanism of hydroformylation of 1-hexene was found to fit with the experimental rate with $\pm 15\%$ deviation.

Keywords: Hydroformylation, Hexagonal mesoporous silica, Kinetics, 1-Hexene

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1. Introduction

Hydroformylation of alkenes used for the synthesis of a wide range of aldehydes is commercially carried out employing rhodium and cobalt based homogeneous catalysts [1-2]. The recovery of the homogeneous catalysts from the product mixture is a tedious and often leads to the loss of valuable catalyst. Using biphasic catalyst is one way to overcome this problem. However, biphasic systems have limitations in terms lower solubility of higher alkenes in the aqueous phase [3]. Therefore, the development of a heterogeneous catalyst is needed that would eliminate the need of catalyst recovery from the product mixture and also would enable its use in fixed bed type reactor. Efforts to heterogenize the homogeneous catalysts on to a solid support have been reported [4-6]. However, loss of activity and leaching of heterogenized catalyst still remained as the reasons for restriction of its commercialization.

We have recently reported a heterogeneous catalyst system of rhodium complex $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated into the pores of hexagonal mesoporous silica (HMS) [7]. The catalyst was found to be active for hydroformylation of $\text{C}_5\text{-C}_{12}$ olefins. The heterogeneous catalyst system [7] has shown better performance in the terms of conversion, turn over frequency and percentage of rhodium loading on the support HMS, in comparison of the other closely related rhodium silica based heterogeneous catalyst systems [7-9] reported for hydroformylation of 1-hexene. Kinetic investigations of a catalytic reaction are important to obtain a systematic analysis of the catalyst system for improvement in its performance as well as optimizing the parameters to commercial level [10]. The kinetics of hydroformylation using different homogeneous catalysts of rhodium phosphine ligands [11-20], arsine ligands [1] and phosphite ligands [21-25] have been reported. But the kinetic investigations of heterogeneous hydroformylation are scanty [26-29]. The aim of present work is to investigate the

kinetics of 1-hexene hydroformylation using $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated hexagonal mesoporous silica (Rh-HMS) as a heterogeneous catalyst to develop a kinetic rate model.

2. Experimental

2.1. Materials

Carbon monoxide (CO , 99.8 %) and hydrogen (H_2 , 99.98 %) were procured from Alchemie Gases and Chemicals Private Limited, India. $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, triphenylphosphine (PPh_3), sodium borohydride (NaBH_4 , 99.98 %) and formaldehyde (HCHO , 34%) were purchased from Sigma-Aldrich, USA. Tetraethylorthosilicate (TEOS) and 1-hexene were purchased from Sigma Aldrich, USA. Hexadecyl amine was procured from Sisco Laboratories, India. All chemicals were used without further purification. The double distilled milli-pore de-ionized water was used during the synthesis.

2.2. Synthesis of the catalyst

The catalyst, $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ encapsulated hexagonal mesoporous silica (Rh-HMS) was synthesized by reported method [7]. $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, Rh-complex was prepared by reported method [30] followed by encapsulation into the pores of HMS. For encapsulation, in a typical synthesis, 0.0027 mol of hexadecyl amine was dissolved in a mixture of 0.0909 mol of ethanol and 0.296 mol of deionised water by stirring with a magnetic stirrer. To this stirring solution 0.07 mmol of the Rh-complex was added. To this suspension 0.01 mol of TEOS was added drop wise. Stirring was continued for 1 h and a pale yellow precipitate was formed, which was kept for 18 h for aging at room temperature. The yellow precipitate was filtered and washed with 1:1 (v/v) ethanol-water mixture and dried in vacuum at room temperature. The detail characterization of

the catalyst was performed by FT-IR, PXRD, surface area analyzer, TGA, ^{31}P CP-MAS NMR, SEM and ICP-AES by using the methodologies and instruments reported in our earlier publication [7].

2.3. Hydroformylation reaction and product analysis

All kinetic experiments were carried out in 100 mL stainless steel autoclave reactor (Autoclave Engineers, USA, model E 01055A) equipped with a controlling unit. In a typical hydroformylation experiment, weighed amount of olefin dissolved in 50 mL of toluene as solvent, with *n*-tridecane as GC internal standard was added to the weighed amount of Rh-HMS in the autoclave reactor. The autoclave was flushed twice with N_2 prior to successively introducing CO and H_2 at a desired pressure. The reactor was then brought to desired reaction temperature. At that time, a sample of the reaction mixture was withdrawn, which was considered as the zero time reading. The hydroformylation reaction was then initiated by starting the stirrer. The reaction was then continued at constant pressure, by supplying CO and H_2 (1:1) from the reservoir vessel. For kinetic studies, liquid samples were withdrawn during the experiment by a sampling valve at fixed time interval. After the set reaction time, the autoclave was then brought to room temperature with the help of a cooling system, and the pressure drops were also noted. The product analysis was carried out using GC (Shimadzu 17A, Japan), having 5 % diphenyl and 95 % dimethyl siloxane universal capillary column (60 m length and 0.32 mm diameter) and flame ionization detector (FID). The initial column temperature was increased from 40 to 200 °C at the rate of 10 °C/min. N_2 gas (3.4 mL/min) was used as a carrier gas. The temperature of injection port and FID were kept constant at 200 °C during product analysis. The retention times for different compounds were determined by injecting pure compounds under identical GC conditions.

2.4. Kinetic analysis

The effect of alkene chain length on the rate of reaction was studied. 1-hexene as a representative alkene was taken for the detailed study on the kinetics of hydroformylation. The parameters like concentration of 1-hexene, amount of catalyst, partial pressure of hydrogen and carbon monoxide and temperature are found to affect on the rate of hydroformylation reaction. Hence these parameters were varied to study the kinetics of the hydroformylation reaction of 1-hexene using Rh-HMS catalyst. *n*-heptanal and 2-methyl hexanal were the major products during the employed reaction conditions.

3. Results and discussion

3.1. Effect of chain length

The effect of the chain length of alkenes on the rate of hydroformylation of 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene and 1-dodecene, were studied by conducting the kinetic experiments under identical chemical and physical conditions by varying these alkenes. The plots of time dependent consumption of C₅ to C₁₀ linear alkenes were made and the concentrations of the alkenes were found to be continuously decreased. The rates were determined from the linear portions of the slopes of the plots of the decreasing concentration of alkenes as given in Eq. 1.

$$\text{Rate} = - d [\text{Alkene}] / dt \quad (1)$$

It was found that the reaction rate was maximum for the lower alkene, 1-pentene. The rate decreased on increasing the chain length as depicted in Fig. 1 with reactivity order of 1-pentene > 1-hexene > 1-heptene > 1-octene > 1-decene, 1-dodecene. The decrease in the rate was observed to be more from 1-pentene to 1-heptene, than those of 1-heptene to 1-dodecene. The rates for 1-decene and 1-dodecene were almost same indicating that on further increasing the chain length, the rates of hydroformylation

were not influenced. It may be explainable in the terms of facile diffusion of lower alkenes into the pore which causes an increase in the rate of reaction. On increasing the chain length the diffusion into pores become difficult and thereby causes lowering the reaction rate. 1-Hexene, having the intermediate effect on the rate of reaction has been taken as representative alkene for the detail kinetic investigations.

3.2. Kinetic profiles for hydroformylation of 1-hexene

The kinetic profile for the hydroformylation of 1-hexene is shown in Fig. 2. A fast consumption of 1-hexene was observed to linearly decrease up to 6 h and after that the consumption became very slow. The rate (v) in terms of the consumption of 1-hexene (Eq. (2)), was determined to be 68.0×10^{-3} M/h.

$$v = -d [1\text{-hexene}] / dt \quad (2)$$

The rate of formation of isomers 2/3-hexene (v_1 , Eq. 3) was increased linearly up to 6 h and after that the formation started decreasing. The rate of formation of 2/3-hexene was 37.5×10^{-3} M/h.

$$v_1 = d [2/3 - \text{hexene}] / dt \quad (3)$$

The formation of n-heptanal (v_2 , Eq. 4) and iso-heptanal (v_3 , Eq. 5) was linearly increased and the rates were 16.9×10^{-3} M/h (v_2) and 9.6×10^{-3} M/h (v_3), respectively.

The rate v_2 was ~ 1.8 times higher than v_3 .

$$v_2 = d [\text{n-heptanal}] / dt \quad (4)$$

$$v_3 = d [\text{iso-heptanal}] / dt \quad (5)$$

The formation of 2-ethyl 3-methyl butanal (v_4 , Eq. 6) from the hydroformylation of 2/3-hexene was observed with very slow rate, 3.6×10^{-3} M/h (v_4).

$$v_4 = d [2\text{-ethyl 3-methyl butanal}] / dt \quad (6)$$

Summation of the formation rates ($v_1 + v_2 + v_3 + v_4 = 67.6 \times 10^{-3}$ M/h) was found to be almost identical with the consumption rate, v (68.0×10^{-3} M/h) indicating a fine balance between the rates of formations and consumption.

3.3 Dependence of the rate on the amount of the catalyst

The effect of the amount of the catalyst on the various rates was studied by varying the amount from 10 to 600 mg and the corresponding results are given in Table 1. The rate of isomerization (v_1) is slightly faster than those of hydroformylations ($v_2 + v_3 + v_4$) at lower amount, 10 mg of catalyst (Entry 1). Due to lower amount of the catalyst (10 mg) hydroformylation is less favored, since the hydroformylation requires a critical minimum concentration of Rh-complex [31], whereas on the other hand isomerization is favored by the HMS [7]. The rate of isomerization (v_1) was increased on increasing the amount of catalyst from 10-100 mg (Entries 1-3) and on further increasing the catalyst amount the rate (v_1) was decreased. The individual rates v_2 , v_3 , v_4 and v as well as total hydroformylation rates ($v_2 + v_3 + v_4$) were increased on increasing the amount of the catalyst (Entries 2-6). A representative plot for the rate (v) vs. the amount of the catalyst given in Fig. 3 passes through origin indicating that the reaction is completely catalytic under the employed reaction conditions. The increase in the rate (v) was observed up to 300 mg of the catalyst and on further increasing in the amount, the rate approached to attain saturation. Similar trends were observed for the rates v_2 , v_3 and v_4 also after 300 mg of the catalyst. The rate data indicated a first order dependence trend in the terms of the catalyst towards lower amounts. In the line of these observations, an amount of 100 mg of the catalyst was considered for the variation of the other parameters to study their effects on the rate of the reaction.

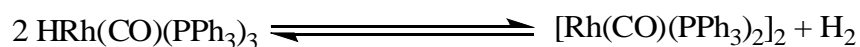
3.4 Dependence of the rate on the concentration of 1-hexene

The effects of the variation of concentration of 1-hexene on the various rates were studied in a wide range of $2.38 \times 10^{-2} - 95.22 \times 10^{-2}$ M, at 40 bar pressure of syn gas ($\text{CO} + \text{H}_2$) and at 80°C with 100 mg catalyst and results are given in Table 2. The rates (v_1 , v_2 , v_3 and v) were increased on increasing the concentration of 1-hexene up to 23.8×10^{-2} M (Entries 1-4) and after that rates were decreased showing substrate inhibition at higher 1-hexene concentration. The formation of 2-ethyl 3-methyl butanal (v_4) was observed from the 23.8×10^{-2} M concentration of 1-hexene and increased on increasing the concentration of 1-hexene. The plot of rate (v) vs. 1-hexene concentration shown in Fig. 4 is indicative of first order dependence in terms of the concentration of 1-hexene towards lower concentration. The trend of increase in rates up to certain concentration of 1-hexene and decrease in rate towards higher concentration are in the agreement with the observations [1, 26, 31] of substrate inhibition kinetics towards higher concentration of alkene indicating a change in the rate determining step. Also from the important reaction steps (Scheme 1) it is clear that the coordination of 1-hexene is an equilibrium step and hence the increase in concentration can favor the backward reaction thus causing a decrease in the rate.

3.5 Dependence of the rate on the partial pressure of hydrogen

The effect of the partial pressure of hydrogen on the various rates, studied in the range of 2-30 bar, with 1-hexene concentration of 47.6×10^{-2} M, amount of catalyst 100 mg, partial pressure of CO 20 bar and at 80°C were given in Table 3. All the rates were increased on increasing the partial pressure of hydrogen. The plot of rate (v) vs. partial pressure of hydrogen is given in Fig. 5. Similar plots were obtained for other rates for hydrogen pressure dependence. The kinetics with respect to the partial pressure of hydrogen was found to follow first order dependence. The first order dependence of the partial pressure of the hydrogen indicated that the oxidative addition of hydrogen to the

acyl complex $(\text{RCO})\text{RhCO}(\text{PPh}_3)_2$ ($\text{R} = \text{alkyl}$) is the rate determining step. At lower partial pressure of H_2 the formation of possible inactive dimeric species contributes towards decreasing the rate [31].



3.6 Dependence of the rate on the partial pressure of carbon monoxide

The dependence of the various rates on the partial pressure of CO has been studied in the range of 2-30 bar at 1-hexene concentration of 47.6×10^{-2} M, amount of catalyst 100 mg, partial pressure of H_2 20 bar and 80°C were given in Table 4. The rates (v_1 , v_2 , v_3 and v) were found to be increased with increase in partial pressure of CO up to 5 bar above which the rate decreased and then became independent of CO pressure. The rate (v_4) was increased on increasing the partial pressure of CO. The Fig. 6 represented the plot of rate (v) vs. the partial pressure of CO indicating that positive order [31] kinetics was followed towards low CO pressure. A rate inhibition on increasing CO partial pressure may be due to the formation of inactive dicarbonyl $[\text{HRh}(\text{acyl})(\text{CO})_2(\text{PPh}_3)_2]$ and tricarbonyl $[\text{HRh}(\text{acyl})(\text{CO})_3(\text{PPh}_3)]$ acyl species [30-31]. Increase in the CO partial pressure is expected to increase the concentration of these inactive di- and tri- carbonyl species, which cause decrease in the rate of reaction.

3.7 Dependence of the rate on temperature

Temperature dependence experiments were conducted in the range of $60\text{--}100^\circ\text{C}$ and the various rates are listed in Table 5. The rates of isomerization (v_1) and hydroformylation (v_2 , v_3 and v_4) and consumption of 1-hexene (v) were increased with temperature. A plot of the dependence of rate (v) on temperature is given in Fig. 7. The activation energy was calculated by considering the rate of consumption of 1-hexene

with temperature using Arrhenius equation. The value of activation energy was found to be 27.89 kJ/mol.

3.8 Kinetic modeling

The kinetic modeling of heterogeneous hydroformylation of alkenes has not been studied extensively. To develop a suitable rate equation, the data analysis should be in kinetic regime with negligible mass transfer effects. For this purpose all the reactions were performed at a stirring speed of 850 rpm so that the reaction takes place in the kinetic regime. For the selection of kinetic models for the rate data fit, it is appropriate to derive a rate equation model from the actual mechanism rather than to derive a semi-empirical model. For this, the possible steps based on actual mechanism of hydroformylation were worked out assuming oxidative addition of hydrogen as the rate determining step. The possible reaction scheme is shown in Scheme 1.

Rate of hydroformylation reaction is given as,

$$\text{rate} = k C_3 [\text{H}_2] \quad (\text{i})$$

and the total concentration of catalyst species is,

$$C = C_1 + C_2 + C_3 + C_4 + C_5 \quad (\text{ii})$$

Applying equilibrium approximation and deriving the rate equation, then equation (i) becomes,

$$\text{rate} = \frac{kK_1K_2[C][1\text{-hexene}][\text{H}_2][\text{CO}]}{1 + K_1[\text{CO}] + K_1K_2[\text{CO}][1\text{-hexene}] + K_1K_2K_3[\text{CO}]^2[1\text{-hexene}] + K_1K_2K_3K_4[\text{CO}]^3[1\text{-hexene}]} \quad (\text{iii})$$

Where K_1 , K_2 , K_3 and K_4 are constants from the steady state equilibrium.

It is easy to calculate the model with homogeneous hydroformylation reaction as all the species involved are in homogeneous phase during the reaction so that the concentration of all species can be calculated. But in the case of heterogeneous reactions the catalyst

is in another phase with respect to all other species. Therefore it is difficult to calculate the concentration of active species associated with it. Hence here we are proposing a method to calculate the rates using the theoretical model as g/lit/h rather than mol/lit/h. Calculated rates were compared with the experimental rates in g/lit/h. The evaluation of rate parameters were done by putting anticipated values for constants by iteration method to get best fit. The experimental data were fitted properly for the parameters 1-hexene concentration, carbon monoxide concentration and hydrogen concentration in equation (iii), but deviations were shown at higher catalytic amounts. The equation fitted well towards lower amount of the catalyst. Eliminating the higher catalyst amounts the model fits within the 15 % error which is within the experimental error for a heterogeneous hydroformylation reaction (Fig. 8).

It is of interest to have a comparative insight in to the kinetic performance of the present Rh-HMS heterogeneous catalyst system with the homogeneous system for the hydroformylation of 1-hexene. Isomerization of 1-hexene is not reported in the homogeneous conditions. The kinetics of hydroformylation of 1-hexene catalyzed by heterogeneous Rh-HMS and reported [31] homogeneous $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ system were compared. The kinetic performance of Rh-HMS for the various parameters like catalyst amount, 1-hexene concentration, partial pressures of CO and H_2 and temperature were found to have almost comparable trend. Similar to the present heterogeneous catalyst system, in homogeneous conditions [31], the rates were increased on increasing the concentration of the catalyst, partial pressure of hydrogen and temperature where as the CO pressure and 1-hexene concentration dependence showed substrate inhibition kinetics. In the line of heterogeneous conditions, the kinetics was first order with respect to partial pressure of hydrogen, catalyst concentration and towards lower

concentration of 1-hexene, and positive order for lower partial pressure of CO in homogeneous conditions [31].

4. Conclusions

HRh(CO)(PPh₃)₃ complex encapsulated in the pores of HMS was synthesized and used to perform the detail kinetic analysis for the hydroformylation of 1-hexene. The rate of hydroformylation increased with the increase in catalyst amount and gets saturated at higher catalyst amount. The rate was first order with partial pressure of hydrogen. But it was inhibited by high concentration of carbon monoxide and 1-hexene. Kinetic model was derived from the known mechanism of hydroformylation and tested for comparison of experimental rates with that of model rates. The rates were calculated in the form of g/lit/h and found to be best fit within the range of experimental error of 15 %.

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Figure Captions

Fig. 1. Effect of alkene chain length on the rate; alkene = 47.6×10^{-2} M, catalyst = 100 mg, $p_{CO} = 20$ bar, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

Fig. 2. Kinetic profile of the consumption of 1-hexene and formation of the products; 1-hexene = 47.6×10^{-2} M, catalyst = 10 mg, $p_{CO} = 20$ bar, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

Fig. 3. Effect of catalyst amount on the rate; 1-hexene = 47.6×10^{-2} M, $p_{CO} = 20$ bar, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

Fig. 4. Effect of 1-hexene concentration on the rate; catalyst = 100 mg, $p_{CO} = 20$ bar, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

Fig. 5. Effect of partial pressure of hydrogen on the rate; 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, $p_{CO} = 20$ bar, $T = 80$ °C, toluene = 50mL

Fig. 6. Effect of partial pressure of CO on the rate; 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

Fig. 7. Effect of temperature on the rate; 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, $p_{H_2} = p_{CO} = 20$ bar, toluene = 50mL

Fig. 8. Comparison of experimental rates with calculated rates from model

Tables

Table 1. Dependence of the rates on the catalyst amount

Entry	Catalyst amount mg	Rate _{2/3-hexene} $v_1 \times 10^2$ M/h	Rate _{n-heptanal} $v_2 \times 10^2$ M/h	Rate _{iso-heptanal} $v_3 \times 10^2$ M/h	Rate _{2-ethyl 3-methyl butanal} $v_4 \times 10^2$ M/h	Rate = (-d[1-hexene]/dt) $v \times 10^2$ M/h
1	10	3.66	1.61	1.16	-	6.48
2	20	5.01	3.00	1.90	0.16	10.25
3	100	12.80	7.95	4.26	0.98	26.85
4	300	11.51	15.20	8.69	2.80	38.36
5	400	9.01	17.85	10.30	3.10	40.85
6	600	7.29	20.97	11.75	3.38	44.35

Reaction conditions: 1-hexene = 47.6×10^{-2} M, pCO = 20 bar, p_{H₂} = 20 bar, T = 80 °C, toluene = 50mL

Table 2. Dependence of the rates on 1-hexene concentration

Entry	1-Hexene concentration M x 10 ²	Rate _{2/3-hexene} v ₁ x 10 ² M/h	Rate _{n-} heptanal v ₂ X 10 ² M/h	Rate _{iso-} heptanal v ₃ X 10 ² M/h	Rate _{2-ethyl} 3-methyl butanal v ₄ X 10 ² M/h	Rate = (-d[1- hexene]/dt) v x 10 ² M/h
1	2.38	6.50	2.01	1.46	-	10.08
2	5.95	11.12	4.52	2.96	-	18.72
3	11.9	14.29	9.42	5.75	-	29.52
4	23.8	17.40	11.51	6.16	0.20	35.39
5	35.7	15.23	8.73	4.6	0.56	29.88
6	47.6	12.80	7.95	4.26	0.98	26.85
7	95.23	10.32	6.52	4.31	1.0	23.76

Reaction conditions: catalyst = 100 mg, pCO = 20 bar, p_{H₂} = 20 bar, T = 80 °C, toluene

= 50mL

Table 3. Dependence of the rates on partial pressure of hydrogen

Entry	H ₂ pressure	Rate _{2/3-hexene} v ₁ x 10 ² M/h	Rate _{n-heptanal} v ₂ x 10 ² M/h	Rate _{iso-heptanal} v ₃ x 10 ² M/h	Rate _{2-ethyl 3- methyl butanal} v ₄ x 10 ² M/h	Rate = (-d[1- hexene]/dt) v x 10 ² M/h
1	2	1.47	0.71	0.31	-	2.5
2	5	4.73	2.06	0.83	-	7.92
3	10	8.12	5.03	1.63	-	14.83
4	20	12.80	7.95	4.26	0.98	26.85
5	30	13.25	17.48	6.86	1.13	38.88

Reaction conditions: 1-hexene = 47.6 x 10⁻² M, catalyst = 100 mg, pCO = 20 bar, T = 80 °C, toluene = 50mL

Table 4. Dependence of the rates on partial pressure of CO

Entry	CO pressure	Rate _{2/3-hexene} $v_1 \times 10^2$ M/h	Rate _{n-heptanal} $v_2 \times 10^2$ M/h	Rate _{iso-heptanal} $v_3 \times 10^2$ M/h	Rate _{2-ethyl 3- methyl butanal} $v_4 \times 10^2$ M/h	Rate = (-d[1- hexene]/dt) $v \times 10^2$ M/h
1	2	51.08	8.10	5.40	0.10	65.50
2	5	72.63	9.80	6.31	0.50	90.00
3	10	57.13	8.32	6.26	0.91	73.80
4	20	12.80	7.95	4.26	0.98	26.85
5	25	12.16	7.62	4.41	1.32	26.35
6	30	12.12	7.31	4.21	1.23	25.20

Reaction conditions: 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, p_{H_2} = 20 bar, T = 80 °C, toluene = 50mL

Table 5. Dependence of rates on temperature

Entry	Temp. °C	Rate _{2/3-hexene} $v_1 \times 10^2$ M/h	Rate _{n-heptanal} $v_2 \times 10^2$ M/h	Rate _{iso-heptanal} $v_3 \times 10^2$ M/h	Rate _{2-ethyl 3- methyl butanal} $v_4 \times 10^2$ M/h	Rate = (-d[1- hexene]/dt) $v \times 10^2$ M/h
1	60	6.19	5.61	2.77	0.41	15.04
2	70	9.82	6.48	3.13	0.62	20.10
3	80	12.80	7.95	4.26	0.98	26.85
4	90	17.19	10.52	6.56	1.32	36.72
5	100	19.61	13.15	7.90	1.71	42.84

Reaction conditions: 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, pCO = 20 bar, p_{H₂} = 20 bar, toluene = 50mL.

Figures

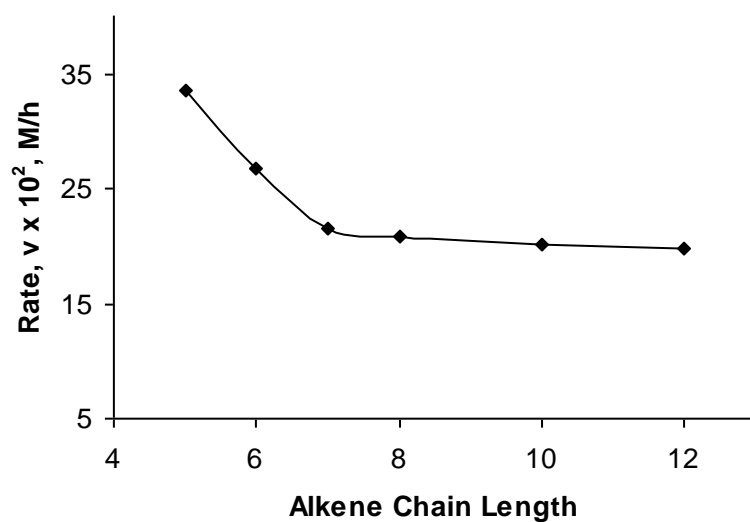


Fig. 1. Effect of alkene chain length on the rate; alkene = 47.6×10^{-2} M, catalyst = 100 mg, pCO = 20 bar, p_{H₂} = 20 bar, T = 80 °C, toluene = 50mL

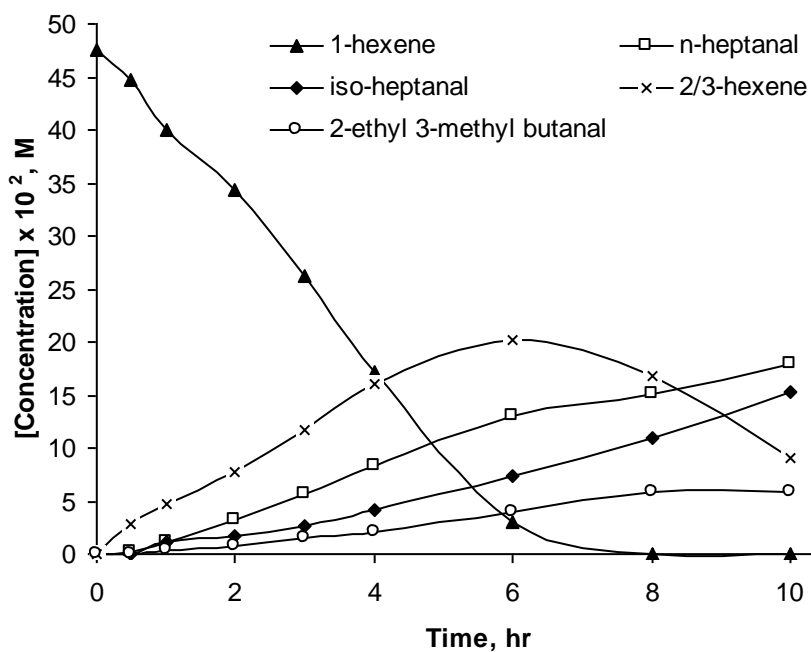


Fig. 2. Kinetic profile of the consumption of 1-hexene and formation of the products; 1-hexene = 47.6×10^{-2} M, catalyst = 10 mg, $p_{CO} = 20$ bar, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

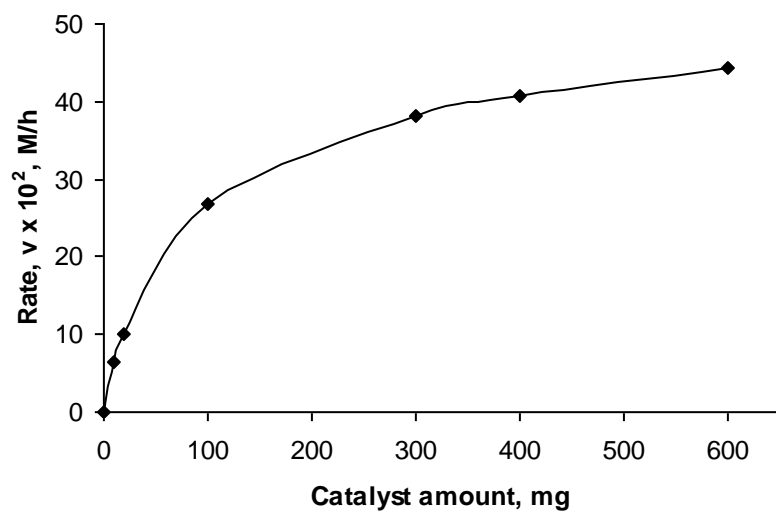


Fig. 3. Effect of catalyst amount on the rate; 1-hexene = 47.6×10^{-2} M, $p_{CO} = 20$ bar, $p_{H_2} = 20$ bar, $T = 80$ °C, toluene = 50mL

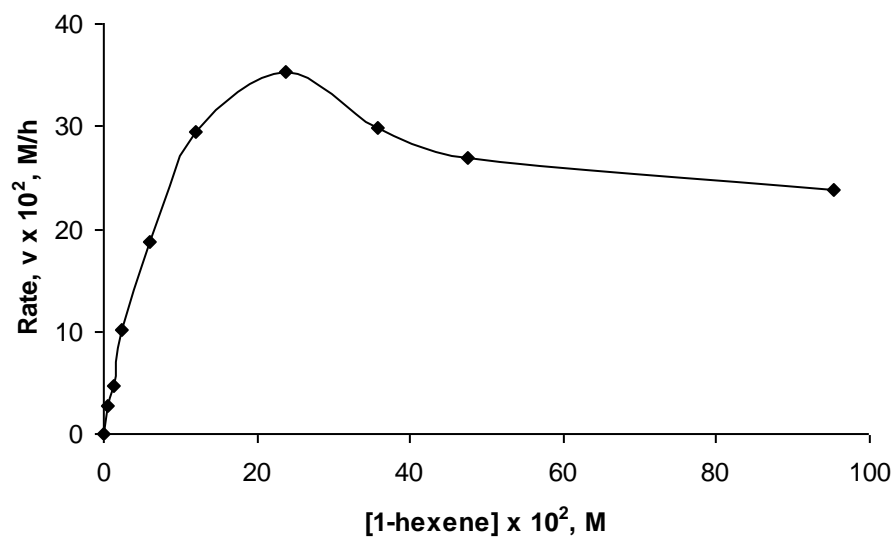


Fig. 4. Effect of 1-hexene concentration on the rate; catalyst = 100 mg, pCO = 20 bar, p_{H₂} = 20 bar, T = 80 °C, toluene = 50mL

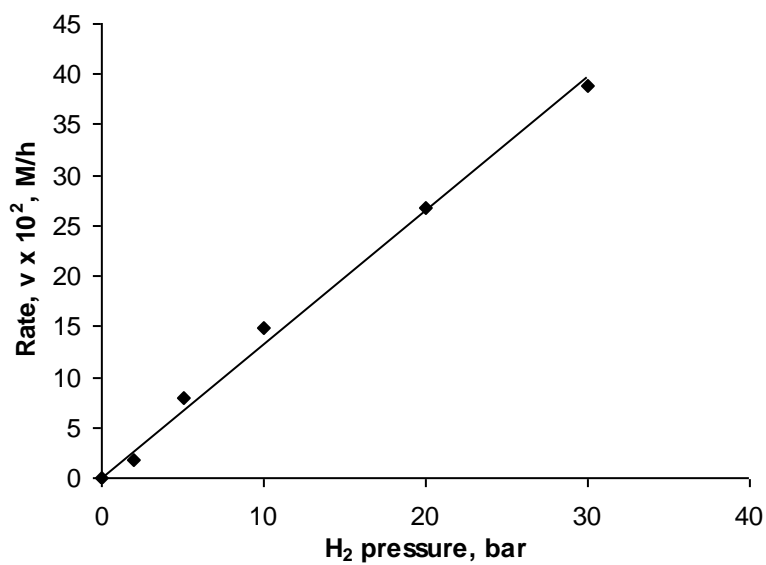


Fig. 5. Effect of partial pressure of hydrogen on the rate; 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, pCO = 20 bar, T = 80 °C, toluene = 50mL

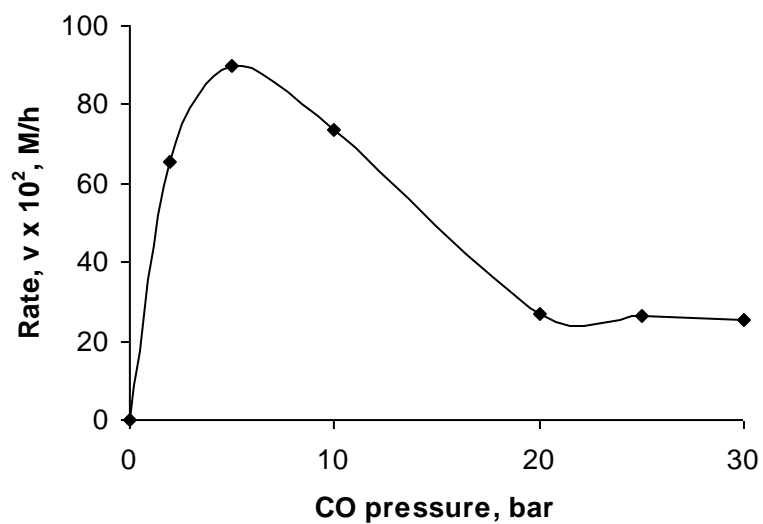


Fig. 6. Effect of partial pressure of CO on the rate; 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, p_{H_2} = 20 bar, T = 80 °C, toluene = 50mL

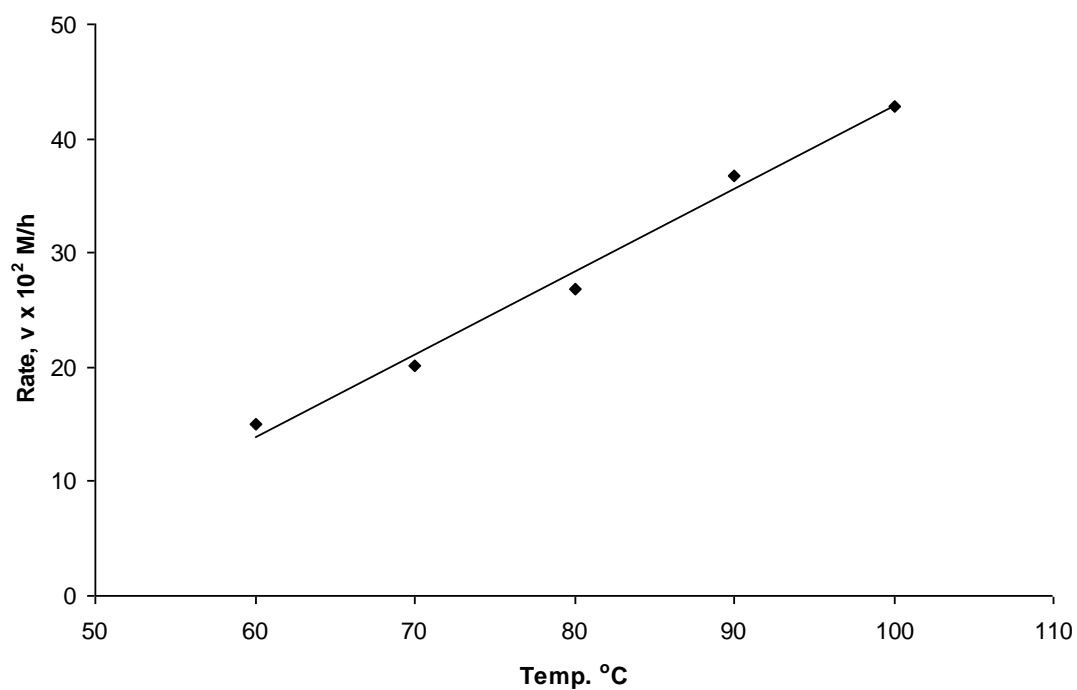


Fig. 7. Effect of temperature on the rate; 1-hexene = 47.6×10^{-2} M, catalyst = 100 mg, $p_{H_2} = p_{CO} = 20$ bar, toluene = 50mL

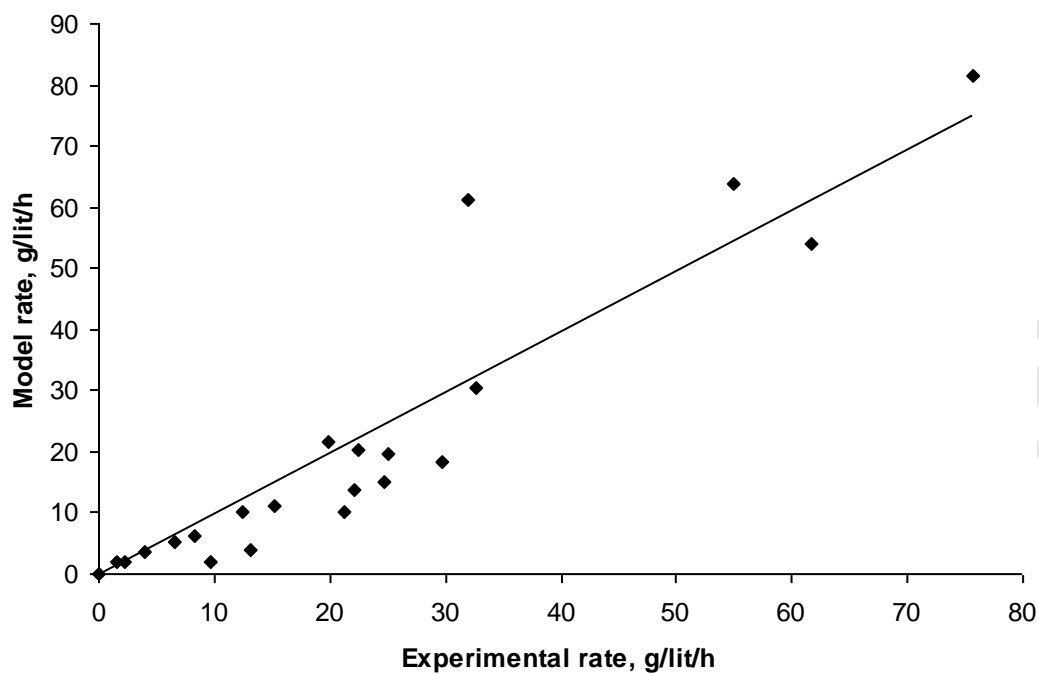
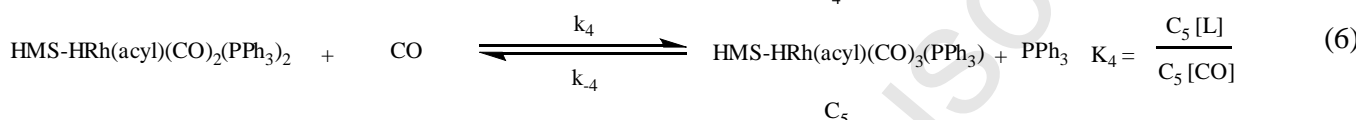
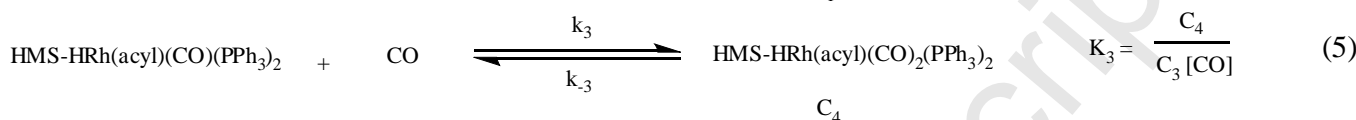
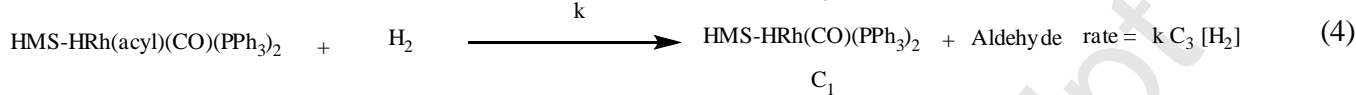
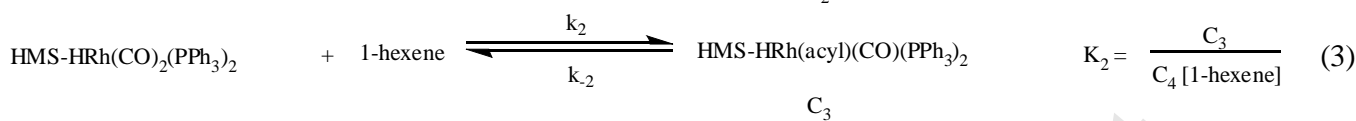
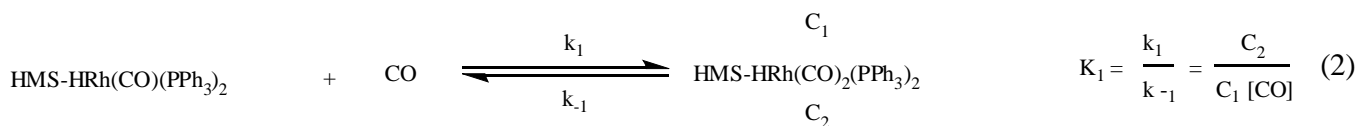
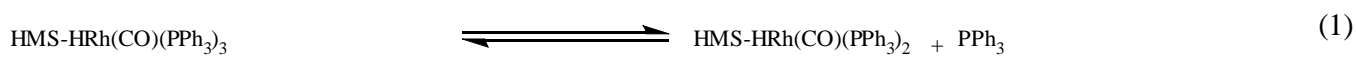


Fig. 8. Comparison of experimental rates with calculated rates from model



Scheme 1. Important reaction steps for heterogeneous hydroformylation of 1-hexene