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# Hydroformylation of propene heterogeneously catalyzed by HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> encapsulated in to hexagonal mesoporous silica—Parametric variation and mass transfer study

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#### ARTICLE INFO

Article history: Received 26 July 2011 Received in revised form 12 October 2011 Accepted 10 December 2011 Available online 19 December 2011

Keywords: Hydroformylation Heterogeneous catalyst Propene Kinetics Mass transfer

#### ABSTRACT

An in situ encapsulated  $HRh(CO)(PPh_3)_3$  in to the pores of hexagonal mesoporous silica (HMS) acting as nanophase reactors, was investigated for the catalytic hydroformylation of propene. The encapsulated catalyst (Rh–HMS) was synthesized and characterized by PXRD, FT-IR, surface area measurements and TEM. The catalyst was effectively active with 99% conversion of propene and 100% selectivity to aldehydes. The effects of reaction parameters: temperature, partial pressure of CO and H<sub>2</sub>, amount of catalyst and HRh(CO)(PPh\_3)\_3 to TEOS ratio on conversion, selectivity and rates were investigated in detail. The rates determined in term of the formation of aldehydes were found to be first order with respect to hydrogen pressure. Catalyst showed first order dependence towards its lower amount. CO pressure variation showed positive order towards lower pressure and inhibition at higher pressures. The investigated mass transfer effects on the kinetics indicated that the reaction runs with negligible mass transfer limitations. The heterogenized Rh–HMS catalyst was effectively recycled for six times.

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#### 1. Introduction

Hydroformylation of olefin is one of the industrially important homogeneously catalyzed reactions [1] and nowadays, the world production approaches 10<sup>7</sup> tons/year [2] by this process. In this, nearly 86% of the total hydroformylation production capacity is based on the propene hydroformylation to give butanals (n- and iso-) as major products [3]. The use of n-butanal is chiefly for the production of C<sub>8</sub>-aldol products such as 2-ethylhexanal and 2ethylhexanol, which are valuable intermediates for the production of dioctylphthalate, other plasticizers, coatings, adhesives, lubricants, alkyd resins and fine chemicals. Iso-butanal is converted to iso-butyl alcohol, neopentyl glycol, iso-butyl acetate, iso-butyric acid, iso-butylidene diurea, methyl iso-amyl ketone and various hydrogenation and esterification products. Monoisobutyrate synthesized by homo-aldol condensation of iso-butanal [4,5] is the most common coalescing agent (used at 0.5-2 vol%) in latex paints. Iso-butyl acetate and iso-butylidene diurea are used as a solvent for nitrocellulose coatings and for slow-release fertilizer respectively [6].

Industrially, hydroformylation process is performed under homogeneous conditions. However, homogeneous system has limitations of the separation and recycling of the catalyst. To overcome these drawbacks investigations are focused on the biphasic catalysis [7,8] and heterogenization of homogeneous catalysts [9–12]. The heterogenization of homogeneous catalysts was reported on the supports like SBA-15 [13], silicate membrane-activated carbon [14], hydrotalcites [15], zeolites [9] and alumina [16]. Hydroformylation of propene had been widely studied by homogeneous [17], heterogeneous [18] and two phase process with a water-soluble ligand modified catalyst [19].

Recently we have reported,  $HRh(CO)(PPh_3)_3$  encapsulated hexagonal mesoporous silica (HMS), as an efficient heterogeneous catalyst for hydroformylation of  $C_5-C_{12}$  olefins [20,21]. Here the investigation is focused for the hydroformylation of lower and gasseous alkene, propene. In heterogeneous catalysts apart from the studies on conversion and selectivity, the detail investigations on the parametric variations, reaction kinetics and mass transfer effects play an important role. Though the reports on parametric studies are available for various substrates, the investigations on the kinetics of hydroformylation of propene over heterogeneous catalysts are paid less attention. Understanding the effects of diffusion leading to mass transfer constraints in heterogeneous conditions is more important and have pressing need to perform

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<sup>0926-860</sup>X/\$ – see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2011.12.017

investigations in these lines. Studies on kinetics and diffusion can significantly contribute towards scaling up the reaction and reactor design.

In the present work, heterogenized HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> (Rhcomplex) in the mesopores of HMS has been investigated for the hydroformylation of propene. Rh-complex was encapsulated in situ into the dodecyl amine reverse micelle in side the pores of HMS at room temperature. The encapsulation was elegant and the catalyst was used as such without removing the surfactant. The catalyst as a whole uses the properties of micelles present inside the pores to improve the stability of the complex. Even though there is no direct linkage between silica surface and rhodium metal center or the ligand, the Rh-complex was entrapped in the micelles present. The catalyst has been investigated in detail to study the effect of various parameters like, temperature, concentration of the catalyst, partial pressure of the gases CO and H<sub>2</sub> and weight ratio of Rh-complex to tetraethylorthosilicate (Rh-complex: TEOS) on the conversion, selectivity and rates of the hydroformylation of propene. The studies on mass transfer effects were performed based on Carberry number and Wheeler-Weisz criterion.

#### 2. Experimental

#### 2.1. Materials

Carbon monoxide (CO, 99.8%), hydrogen (H<sub>2</sub>, 99.98%) and propene (C<sub>3</sub>H<sub>6</sub>, 99.8%) were obtained from Alchemie Gases and Chemicals Private Limited, India. The rhodium metal precursors RhCl<sub>3</sub>·3H<sub>2</sub>O, triphenylphosphine (PPh<sub>3</sub>), sodium borohydride (NaBH<sub>4</sub>, 99.98%) and formaldehyde (HCHO, 34%) were purchased from Sigma–Aldrich, USA for the synthesis of Rh-complex. Tetraethylorthosilicate (TEOS), dodecyl amine were purchased from Sigma–Aldrich, USA. Solvents were purchased from Qualigens chemicals, India. All chemicals were used without any further purification. The double distilled milli-pore de-ionized water was always used during the synthesis.

#### 2.2. Synthesis of Rh-complex-HMS (Rh-HMS) catalyst

The Rh-complex [22] and HMS [23] have been prepared by reported methods. In a typical synthesis of HMS, 0.0027 mol of dodecyl amine was dissolved in a mixture of 0.0909 mol ethanol and 0.296 mol deionized water. In our previous report we had used hexadecyl amine as template [20] which is replaced here by dodecyl amine due to its easy miscibility with water and ethanol. The solution was stirred at room temperature (RT) on a magnetic stirrer. To this solution 0.01 mol TEOS was added dropwise with vigorous stirring and mixture was stirred for 1 h at room temperature. After 1 h, the white gel precipitate formed was kept at RT for 18 h of aging. The material was filtered and dried in vacuum at RT.

For the synthesis of Rh–HMS, the in situ encapsulation of the Rh-complex into the HMS pores was done, in which 0.0027 mol of dodecyl amine was dissolved in a mixture of 0.0909 mol of ethanol and 0.296 mol of deionized water. The solution was stirred on a magnetic stirrer and in that 0.07 mmol of the Rh-complex was added. To this suspension 0.01 mol of TEOS was added dropwise with vigorous stirring. The stirring was continued for 1 h and a pale yellow precipitate was formed, which was kept for 18 h for aging at RT. The yellow precipitate was filtered and dried in vacuum at room temperature.

The role of the surfactant is to heterogenize Rh-complex inside the pores thereby avoiding the need of functionalization of the support. In this heterogenized catalyst system, the Rh-complex entrapped in the micelles can also act as a homogeneous catalyst inside the pores. Each pore, containing surfactant reverse micelles and Rh-complex, can act as a nanophase reactor. Further more, the surfactant present can improve the solubility of the olefin inside the pores by which a higher contact with metal center can be achieved.

#### 2.3. Characterization techniques

The FT-IR spectra of the samples were recorded from 400 to  $4000 \text{ cm}^{-1}$  with a Perkin–Elmer Spectrum GX FT-IR system using KBr pellets. Powder X-ray diffraction (PXRD) patterns of the catalyst samples were done by Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered Cu-K $\alpha$  radiation ( $\lambda = 1.54050 \text{ Å}$ ) over a  $2\theta$  range of  $1-10^{\circ}$  at a step time of  $0.05^{\circ} \text{ s}^{-1}$ . The surface area and pore size distribution of the samples were measured by nitrogen adsorption at 77.4 K using a Sorptometer (ASAP-2010, Micromeritics). All the samples were degassed at 80 °C for 4 h prior to the measurements. Morphology of the catalyst was measured using a TEM, 200KV (JEOL, JEM 2100) equipped with EDX facility. Rhodium elemental analysis was carried out with ICP-AES (Perkin–Elmer, Optima 2000).

#### 2.4. Hydroformylation reaction

The hydroformylation experiments were carried out in a 100 ml autoclave equipped with a mechanical stirrer at a stirring speed of 950 rpm. In the typical experiments, desired amount of Rh-HMS catalyst in toluene and decane as GC internal standard were added into the autoclave. After sealing, the autoclave was flushed twice with N<sub>2</sub>. After flushing, propene, carbon monoxide and hydrogen gases were charged at desired pressures. The reactor was then brought to desired reaction temperature. After the reaction, the reactor was cooled down by supplying water inside the coil and reaction vessel was placed in the ice bath. The product analysis was carried out using Gas Chromatography (GC) (Shimadzu 17A, Japan) and GC-MS (Schimadzu QP-2010, Japan). To ensure the reproducibility of the reaction, repeated experiments were carried out under identical reaction conditions. The results obtained, including conversion and selectivity was found to be in the range of 5% variation. Hydroformylation reactions were done in the specially made high-pressure laboratory having safety precautions for using carbon monoxide and conducting reactions at high pressure and temperature. A carbon monoxide gas detector system equipped with alarm, sensing for human tolerance limit of CO, is kept in the laboratory to avoid CO inhaling.

#### 3. Results and discussion

#### 3.1. Characterization of the catalyst

The FT-IR spectra of Rh–HMS and HMS are given in Fig. 1. The FT-IR spectrum of HMS showed the characteristic band at 1073 cm<sup>-1</sup> for asymmetric stretching of Si–O–Si and 798 cm<sup>-1</sup> for tetrahedral SiO<sub>4</sub> structural units. The bands at 2926, 2856 and 1470 cm<sup>-1</sup> are assigned to C–H asymmetric stretching, C–H symmetric stretching and NH<sub>2</sub> scissor respectively, of the organic template of dodecyl amine present in pores of the catalyst. Rh–HMS showed extra distinguishable  $\nu_{Rh-CO}$  and  $\nu_{Rh-P}$  bands at 1920 cm<sup>-1</sup> and 693 cm<sup>-1</sup> respectively [24] evidencing the encapsulation of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> in to the pore of HMS. The band at 3438 cm<sup>-1</sup> corresponds to the surface hydroxyl group and –NH<sub>2</sub> stretching vibrations.

As shown in Fig. 2, the powder X-ray diffraction patterns for HMS and Rh–HMS are nearly identical and all materials showed a single diffraction peak ~2.3° of  $2\theta$  corresponding to  $d_{100}$  spacing [23] of 3.5 and 3.6 nm, respectively. The diffuse scattering was observed at ~5° and is attributed due to *hkl* reflections that are broadened as a result of small crystalline domain effects. The observed similar kind of PXRD pattern for Rh–HMS with that of HMS showed that the HMS



Fig. 1. FT-IR spectra of Rh-HMS, HMS.



Fig. 2. Powder X-ray diffraction pattern of HMS, Rh-HMS.

matrix is retained after encapsulation. The higher intensity peak for HMS got decreased on encapsulation of Rh-complex, indicating that the pores have been filled with the complex.

 $N_2$  adsorption-desorption isotherm of Rh-HMS given in Fig. 3 showed the isotherm of type IV according to BDDT classification [25]. The surface areas of the as synthesized HMS (isotherm not shown in Fig. 3) and Rh-HMS were  $276 \text{ m}^2/\text{g}$  and  $28 \text{ m}^2/\text{g}$  respectively. The size of the pores, determined from pore size distribution curves is 3.93 and 5.7 nm for the as synthesized HMS and Rh-HMS respectively. The expansion in pore diameter and decrease in surface area for Rh-HMS are due to the presence of bulky Rh-complex



Fig. 3. N<sub>2</sub> adsorption-desorption isotherm of Rh-HMS, HMS.



Fig. 4. <sup>31</sup>P-CPMAS NMR of Rh-HMS.

inside the pores of HMS. The pore volume of HMS and Rh–HMS were 0.21 and 0.031 cm<sup>3</sup>/g respectively. The pore volume was decreased by pore filling with the complex. The presence of micropores was also observed in the adsorption and hysterisis of Rh–HMS at lower relative pressures. This may be due to the presence of some amount of Rh-complex on the surface, which may be adsorbed on the pore opening making the effective pore diameter smaller, in the range of micro pores.

The <sup>31</sup>P-CPMAS NMR of Rh–HMS is shown in Fig. 4. There are two main peaks at 46.1 and 36.8 ppm corresponding to the phosphorous in the encapsulated complex. The existence of two peaks is due to the experienced geometrical constraints in the solid state by the complex in encapsulated state. This geometrical constraint makes one of the Rh–P to have a different bond angle than the other two P atoms leading to a distorted octahedral HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> complex. This phosphorous having different bond angle have a chemical shift to higher ppm value. A peak at -4.6 ppm corresponds to the free PPh<sub>3</sub> ligand dissociated during encapsulation.

The TEM image of the Rh–HMS given in Fig. 5 showed the hexagonal array of mesoporous structure of the catalyst corresponding to HMS. Elemental analysis by ICP showed that the catalyst contains 0.62 wt% of rhodium.



Fig. 5. TEM image of Rh-HMS.

Table 1
Effect of catalyst amount on propene hydroformylation.

Entry	Catalyst amount (mg)	Time (h)	Conversion (%)	iso-butanal	n-butanal	n/iso ratio
4	15	2	18.92	55.34	44.66	0.81
1	15	10	98.11	55.58	44.42	0.80
	50	2	26.21	54.56	45.44	0.83
2	50	10	98.23	55.11	44.89	0.81
		2	35.12	56.02	43.98	0.78
3	100	7	98.68	55.91	44.09	0.79
		2	47.40	57.31	42.69	0.74
4	200	7	100	57.95	42.05	0.72
_		2	58.92	62.45	37.55	0.60
5	400	7	100	61.93	38.07	0.61
		2	71.29	64.80	35.20	0.54
6	800	5	100	64.91	35.09	0.54

Reaction conditions: propene = 7 bar, syngas = 40 bar, temp. =  $110 \degree$ C, toluene = 50 mL, and agitation speed = 950 rpm.

#### 3.2. Hydroformylation of propene

The catalyst was found to be active for hydroformylation of propene with 100% selectivity to aldehydes. The n/iso ratio of the products was in the range of 0.65–0.9. No hydrogenation product, propane, was observed under the employed reaction conditions. The reason may be that for propene the HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> complex is more active for CO addition and thus it favors the formation of aldehydes. The catalyst was studied to observe the effect of the reaction parameters: catalyst amount, HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> to TEOS ratio, temperature, partial pressure of H<sub>2</sub> and CO on the conversion, selectivity and rates.

#### 3.2.1. Effect of catalyst amount on propene hydroformylation

The effect of the catalyst amount in the wide range of 15–800 mg was studied on the hydroformylation of propene at constant syngas pressure (40 bar, 1:1) and temperature 110 °C and the results are listed in Table 1. The pronounced effect was observed at lower reaction time on the conversion and selectivity. The conversion was increased from 18.92 to 71.29% at 2 h on increasing the catalyst amount from 15 to 800 mg. The selectivity at 2 h for iso-butanal was increased from 55.34 to 64.80% with a drop in n/iso ratio of 0.81–0.54 on increasing the catalyst amount from 15 to 800 mg. For lower catalyst amounts up to 50 mg, the time required for >98% conversion was 10 h and was reduced to 7 h for 100 mg. Time got reduced to 5 h for 800 mg of the catalyst for 100% conversion. The results indicated that on increasing the catalyst amount both conversion and selectivity for the formation of iso-butanal were increased and the selectivity for n-butanal was decreased.

A representative time dependent product formation kinetic profile is given in Fig. 6. Similar plots of concentration vs. time were made and the rates (Eqs. (1) and (2)) were calculated from the slopes of the early linear portions of the formation of iso- and n-butanal.

Rate of formation of n-butanal,

$$v_1 = \frac{d[\text{n-butanal}]}{dt} \tag{1}$$

Rate of formation of iso-butanal,

$$v_2 = \frac{d[\text{iso-butanal}]}{dt} \tag{2}$$

The effects of the catalyst amount on the rates of the formation of n-butanal ( $v_1$ ) and iso-butanal ( $v_2$ ) are shown in Fig. 7. The rate of formation of iso-butanal was more than that of n-butanal. Both the rates  $v_1$  and  $v_2$  were linearly increased up to 200 mg of the catalyst and on further increasing the catalyst amount the rates started to approach saturation. For all the studied catalyst amounts the



Fig. 6. Time dependent formation of product.

rate of formation of iso-butanal was higher than that of n-butanal. Towards lower amount of the catalyst a first order kinetics was observed in terms of the formation of butanal.

## 3.2.2. Effect of Rh-complex: TEOS ratio on the propene hydroformylation

In order to study the effect of Rh-complex: TEOS ratio on the hydroformylation of propene the catalyst with different amount of rhodium to TEOS ratios: 1, 3, 6, and 12% were prepared and their results are listed in Table 2. On increasing the amount of Rh-complex the conversion was increased. The selectivity to isobutanal was decreased with increase in n-butanal on increasing



Fig. 7. Effect of amount of catalyst of on the rate of propene hydroformylation.

Entry	Rh-complex to TEOS (wt)	Time (h)	Conversion (%)	iso-butanal	n-butanal	n/iso ratio
1	1	2	36.21	57.87	42.13	0.73
1	1	7	98.03	59.18	40.82	0.69
2	3	2	47.40	57.31	42.69	0.74
2	5	7	100	57.95	42.05	0.72
3	6	2	76.97	53.89	46.11	0.85
5	0	5	100	54.68	45.32	0.83
4	12	2	98.37	51.09	48.91	0.96
т	12	3	100	51.02	48.98	0.96

 Table 2

 Effect of Rh-complex to TEOS ratio on propene hydroformylation.

Reaction conditions: catalyst = 200 mg, propene = 7 bar, pCO = 20 bar,  $pH_2 = 20$  bar, temp. = 110 °C, toluene = 50 mL and agitation speed = 950 rpm.



Fig. 8. Effect of temperature on the rate of propene hydroformylation.

the ratio. Moreover above 3% of Rh-complex to TEOS ratio the reaction was completed within 5 h. The observed increase in selectivity of n-butanal on increasing the Rh-complex to TEOS ratio was different with that of increasing the catalyst amount (Table 1). This change in selectivity may be attributed to the fact that at higher Rh-complex to TEOS ratio, the possibility of Rh-complex being on the surface of HMS is higher than that are encapsulated in the pores. These surface adsorbed Rh-complex can get leached out easily and act as a homogeneous catalyst under the employed experimental conditions leading to higher selectivity to n-butanal.

#### 3.2.3. Effect of temperature on propene hydroformylation

The effect of temperature on the conversion and selectivity of the products of propene hydroformylation was investigated at constant catalyst amount (200 mg) and syngas pressure (40 bar, 1:1) and the results are given in Table 3. Conversion was increased from 55.95 to 100% on increasing the temperature from 70 to 120 °C. The selectivity showed that on increasing the temperature the formation of iso-butanal increased. This led to a drop in n/iso ratio on increase of the temperature. Effect of temperature on the rates  $v_1$  and  $v_2$  were studied in the range of 70–110 °C and the corresponding results are given in Fig. 8. The rates were increased on increasing the temperature. At 70 °C the rates of formation of iso

and n-butanal were almost same. On increasing the temperature rates of iso-butanal were more increased than that of n-butanal. This increase in rate of iso-butanal resulted in the high selectivity of iso-butanal at higher temperature. The curved nature of the rate plot of iso-butanal indicates that there is a possible shift in the mechanism at higher temperature which leads to the higher formation of iso-butanal.

## 3.2.4. Effect of partial pressure of $H_2$ on propene hydroformylation

The results on the effect of partial pressures of H<sub>2</sub> on the hydroformylation of propene are given in Table 4. On increasing the partial pressures of H<sub>2</sub>, the conversion was increased. For lower time of 2 h, the conversion 29.97% at  $pH_2$  of 10 bar was increased to 47.4% at 20 bar and further increased to 100% at 40 bar. At higher time of 7 h, the conversion was 83.37% for  $pH_2$  of 10 bar and increased to 100% at 20 bar. When the partial pressure of H<sub>2</sub> was increased to 30 bar and above, hydroformylation was completed with 100% conversion in lower reaction time (entry 5, 6). The lower conversion at lower partial pressures of H<sub>2</sub> is assignable for insufficient hydrogen concentration and the formation of possible dimeric species [22] of Rh-complex, [Rh(CO)(PPh<sub>3</sub>)<sub>3</sub>]<sub>2</sub>. The formation of such species caused a reduction in the active catalytic species decreasing the total catalytic activity. The partial pressure of H<sub>2</sub> also had influential effect on the selectivity of n- and iso-butanal. As the *p*H<sub>2</sub> is increased, the selectivity to n-butanal was increased. The selectivity for n-butanal was 40.38% at pH<sub>2</sub> of 10 bar with n/iso ratio of 0.68 which was increased to 47.23% at 40 bar with a n/iso ratio of 0.89.

The effect of partial pressure of hydrogen on  $v_1$  and  $v_2$  are shown in Fig. 9. Both the rates  $v_1$  and  $v_2$  were increased on increasing the hydrogen pressure showing first order dependence in hydrogen pressure. For hydroformylation reactions, the oxidative addition of hydrogen is the rate-determining step and in those cases the dependency of rate with  $pH_2$  shows a first order dependence [21].

## *3.2.5. Effect of partial pressure of CO on propene hydroformylation*

Partial pressure of CO was varied from 15 to 35 bar and the results are listed in Table 5. Typical CO partial pressure dependence was observed on the conversion and selectivity for lower (2 h) and

#### Table 3

Effect of temperature on propene hydroformylation.

	1 1 9	,				
Entry	Temp. (°C)	Conversion (%)	Time (h)	iso-butanal	n-butanal	n/iso ratio
1	70	55.95	7	50.59	49.41	0.98
2	80	97.50	7	52.93	47.07	0.90
3	90	96.03	7	55.50	44.50	0.80
4	100	98.91	7	55.75	44.25	0.77
5	110	100	7	57.95	42.05	0.72
6	120	100	7	59.98	40.02	0.67

Reaction conditions: catalyst = 200 mg, propene = 7 bar, pCO = 20 bar,  $pH_2 = 20$  bar, toluene = 50 mL and agitation speed = 950 rpm.

Table 4	
Effect of $pH_2$ on	propene hydroformylation.

Entry	$pH_2$ (bar)	Time (h)	Conversion (%)	iso-butanal	n-butanal	n/iso ratio
1	10	2 7	29.97 83.37	59.62 61.76	40.38 38.24	0.68 0.62
2	15	2 7	36.55 97.73	58.20 60.31	41.80 39.69	0.72 0.66
3	20	2 7	47.40 100	57.31 57.95	42.69 42.05	0.74 0.72
4	25	2 7	55.80 100	56.11 57.89	43.89 42.11	0.78 0.73
5	30	2 5	94.91 100	55.23 55.83	44.77 44.17	0.81 0.79
6	40	2	100	52.77	47.23	0.89

Reaction conditions: catalyst = 200 mg, propene = 7 bar, pCO = 20 bar, temp. = 110 °C, toluene = 50 mL and agitation speed = 950 rpm.



Fig. 9. Effect of partial pressure of hydrogen on the rate of propene hydroformylation.

higher (7 h) reaction time. The conversion for 2 h was increased on increasing the partial pressure of CO from 15 (45.56%) to 20 bar (47.40%). On further increasing the partial pressure the conversion was decreased from 47.40 (20 bar) to 31.64% (35 bar) at 2 h. This trend is observed because at high partial pressure of CO, inactive di- and tricarbonylacylrhodium species are formed [21], which cause the drop in the activity. For higher time of 7 h, the conversion was 96.29% for *p*CO of 15 bar which increased to 100% at 20 bar. But higher *p*CO above 25 bar showed a decrease in conversion to 97.20% at 30 bar and 88.61% at 35 bar. The selectivity to n-butanal was decreased on increasing the partial pressure of CO up to 25 bar and then increased slightly. The n/iso ratio was 0.76 at 15 bar and decreased to 0.68 at 25 bar then increased to 0.75 at 35 bar for 2 h of reaction time.

Table 5	
Effect of pCO on propene	hydroformylation.



Fig. 10. Effect of partial pressure of carbon monoxide on the rate of propene hydroformylation.

The effect of partial pressure of carbon monoxide on the rates given in Fig. 10 indicated that both the rates  $v_1$  and  $v_2$  gave increasing trend towards lower pressure. On increasing the partial pressure of CO, after 20 bar, the rates were found to be inversely dependent on the CO partial pressure. At lower CO pressure a positive dependence is observed, pertaining to enhanced formation of active catalytic species HRh(CO)(PPh<sub>3</sub>)<sub>2</sub>. Hence towards lower pressure a positive order and at higher pressures negative order were observed with respect to the partial pressure of CO.

#### 3.2.6. Catalyst recycling for propene hydroformylation

The catalyst was recycled six times at 110 °C and the corresponding results are given in Table 6. The results indicated that there is no

Entry	pCO (bar)	Time (h)	Conversion (%)	iso-butanal	n-butanal	n/iso ratio
	15	2	45.56	56.91	43.09	0.76
1	15	7	96.29	57.15	42.85	0.75
2	20	2	47.40	57.31	42.69	0.74
3	20	7	100	57.95	42.05	0.72
		2	46.18	59.40	40.59	0.68
3	25	7	100	58.81	41.19	0.70
		2	44.01	58.67	41.33	0.70
4	30	7	97.20	58.80	41.20	0.70
_		2	31.64	57.17	42.83	0.75
5	35	7	88.61	58.54	41.46	0.71

Reaction conditions: catalyst = 200 mg, propene = 7 bar,  $pH_2 = 20$  bar, temp. =  $110 \degree C$ , toluene =  $50 \ mL$  and agitation speed =  $950 \ rpm$ .

Table 6	
Recycling of Rh-HMS catal	yst.

Entry	Recycle run	Conversion (%)	% selectivity		n/iso ratio
			iso-butanal	n-butanal	
1	Fresh	100	57.95	42.05	0.72
2	First	98.76	57.65	42.35	0.73
3	Second	98.97	57.08	42.92	0.75
4	Third	97.83	56.54	43.46	0.77
5	Fourth	96.96	56.47	43.53	0.77
6	Fifth	96.85	56.51	43.49	0.77
7	Sixth	96.89	56.43	43.57	0.77

Reaction conditions: propene = 7 bar, catalyst = 200 mg (Rh-complex: TEOS = 3 wt%), pCO = 20 bar, pH<sub>2</sub> = 20 bar, temp. = 110 °C, toluene = 50 mL and agitation speed = 950 rpm.

considerable decrease in conversion and selectivity. The ICP analysis carried out for the organic phase showed that around 5% of the rhodium was leached during the first cycle. This leaching may be due to the weakly adsorbed complex on the outer surface of HMS. The ICP analysis after the second recycle gave only 0.05% rhodium indicating that the encapsulation was stable and leaching occurred from the surface. To confirm that the Rh-complex was not leached out, the ICP analysis of sixth recycled catalyst was done. It showed that 0.57 wt% of Rh was present in the system, showing that an overall ~8% Rh content was lost in the catalyst during recycles. Out of these the 5% of the Rh was lost during the first recycle itself, which arise from the leaching of surface adsorbed Rh-complex. No peak corresponding to dodecyl amine template was found in GC and GC–MS chromatograms of the product mixture which ensured that template micelles were quite stable inside the pores.

#### 3.3. Mass transfer effects

Experiments were carried out to observe the effect of agitation speed on the rate of hydroformylation and the results are given in Table 7. The rates of formation of n- and iso-butanal were low at lower agitation speed. The rates were increased on increasing the stirring speed and attained saturation above 750 rpm. This indicated that the used agitation speed of 950 rpm under the employed conditions of the reaction is in the kinetic regime with negligible mass transfer limitations.

In a heterogeneously catalyzed hydroformylation there are two diffusion factors that can affect the kinetics. The external mass transfer is for the liquid/solid interface and internal mass transfer for the diffusion into the pores. These mass transfer limitations should be negligible for the reaction to be not diffusion controlled. The use of Carberry number (Ca) and Wheeler–Weisz criterion  $(\eta\phi^2)$  are taken into consideration to study the effects of mass transfer on the kinetics [26,27]. The Carberry number gives the extent of external mass transfer limitations and Wheeler–Weisz criterion gives the extent of internal mass transfer limitations.

Table 7
Dependence of agitation speed on the rate of hydroformylation.

Entry	Agitation speed (rpm)	$Rate  imes 10^4 (M/m)$	in)
		iso-butanal	n-butanal
1	250	4.21	3.32
2	500	6.48	4.12
3	750	7.07	5.26
4	950	7.08	5.25
5	1100	7.10	5.25

Reaction conditions: propene = 7 bar, catalyst = 200 mg (Rh-complex: TEOS = 3 wt%), pCO = 20 bar,  $pH_2 = 20 \text{ bar}$ , temp. =  $110 \degree$ C, toluene = 50 mL.

Assuming that the Rh–HMS catalyst particles are spherical, Carberry number for a spherical catalyst particle is given by Eq. (3).

$$Ca = \frac{Rate_{obs}d_p\rho_p}{6k_f C_o w}$$
(3)

Wheeler-Weisz criterion is given by,

$$\eta \phi^2 = \frac{\text{Rate}_{\text{obs}} d_p^2}{4V_{\text{r}} C_{\text{o}} D_{\text{eff}}}$$

The physico-chemical data obtained for the calculation of the Carberry number and Wheeler–Weisz criterion are given in Table 8. The Carberry number with a value less than 0.05 indicates that the reaction proceeds with negligible external mass transfer limitation. When the Wheeler–Weisz factor  $(\eta \phi^2)$  is less than 1, the kinetics of reaction is not influenced by the pore diffusion; the reaction goes with negligible internal mass transfer limitations [26]. The value obtained for Ca and  $\eta \phi^2$  are  $3.103 \times 10^{-9}$  and  $7.75 \times 10^{-6}$  respectively. The values being low were indicative of the negligible mass transfer limitation on the rates of formation of n- and iso-butanal by propene hydroformylation over Rh–HMS catalyst.

From the studies on parametric optimization, kinetics and mass transfer, it is of interest to study for any possible decline of reaction freedom on attacking directions of the propene substrate in the mesopores of Rh-HMS containing dodecylamine reverse micelles and Rh-complex. In the present heterogeneous catalyst system using Rh-HMS, no additional ligand (PPh<sub>3</sub>) is added during the reaction. Also dissociation of some amount of PPh<sub>3</sub> is possible during heterogenization process. Therefore the steric crowd around the Rh metal center is obviously not due to the PPh<sub>3</sub> ligand. In homogeneous hydroformylation, the addition of excess ligands is used to create hindrance around the central metal (e.g. Rh). The steric hindrance created by PPh3 will decrease the reactant freedom of attacking directions which influences the activity and selectivity [31]. The addition of excess PPh<sub>3</sub> ligand in homogeneous hydroformylation decreases the activity but increases the selectivity to n-aldehyde.

In the case of Rh–HMS, there is dodecylamine reverse micelles inside the pores with Rh-complex. The  $-NH_2$  of the dodecylamine may have an affinity towards the Rh of the Rh-complex, but the dodecylamine is lesser steric molecule than PPh<sub>3</sub> for the coordination of propene to the Rh center. The lesser steric hindrance causes weaker anti-Markownikov addition [32] and the electronic effects of  $-NH_2$  (if any coordinated to Rh) results in the higher formation of branch aldehyde [33] and thus causing a decrease in n/iso ratio. Also from the mass transfer calculations it is clear that there is no considerable diffusion limitation during hydroformylation of propene. The presence of dodecylamine reverse micelles is not able to create any steric hindrance on the propene to diffuse and find the Rh center. This low hindrance open all the possible ways of attacking for propene and the reaction proceeds to give low n/iso ratio.

#### Table 8

Physico-chemical data for mass transfer calculations.

Symbol	Quantity	Value	Dimension
Т	Temperature	383	K
Co	Concentration of propene	44.64	mole m <sup>-3</sup>
Vr	Reaction volume	$50  imes 10^{-6}$	m <sup>3</sup>
w	Catalyst weight	$0.2  imes 10^{-3}$	kg
$d_{\rm p}$	Average particle diameter	$1.5  imes 10^{-6}$	m
$ ho_{ m p}$	Particle density	186.25	kg m <sup>−3</sup>
$\mu_{s}$	Viscosity of toluene at T	$0.247  imes 10^{-3}$	Pa s
$ ho_{ m s}$	Density of toluene at T	794.2	kg m <sup>−3</sup>
Ms	Molecular weight of toluene	92.14	g mole <sup>-1</sup>
$\phi_{s}$	Association factor for toluene	1	
Ν	Stirring revolutions	15.83	$s^{-1}$
Sd	Characteristic length of stirrer	$2.1 \times 10^{-2}$	m
V <sub>A</sub>	Molar volume of propene at normal boiling point [28]	68.8	cm <sup>3</sup> mole <sup>-1</sup>
$D = \frac{7.4 \times 10^{-12} (\phi_{\rm S} M_{\rm S})^{1/2} T}{10^{-12} (\phi_{\rm S} (V_{\rm S})^{0.6})^{1/2}}$	Diffusivity ( $\mu_s$ in cP, $V_A$ in cm <sup>3</sup> mole <sup>-1</sup> , T in K) [29]	$8.7\times10^{-9}$	$\mathrm{m}^2\mathrm{s}^{-1}$
$Re = \frac{\rho_s N S_d^2}{\mu_s}$	Reynolds number	22446	
$Sc = \frac{\mu_s}{\rho_s D}$	Schmidt number	35.7	
$Sh = 2 + 0.6 Re^{1/2} Sc^{1/3}$	Sherwood number [30]	297.9	
$k_{\rm f} = \frac{{\rm Sh}D}{d}$	Mass transfer coefficient	1.727	${ m ms^{-1}}$
Robs	Experimental rate $(v_1 + v_2)$	$1.0275  imes 10^{-6}$	mole s <sup>-1</sup>
$Ca = \frac{Rate_{obs}d_p \rho_p}{6k_s C_o w}$	Carberry number	$3.103\times10^{-9}$	
$\theta$ $\theta$	Porosity	0.00577	
τ	Tortuosity factor	1.5	
$D_{ m eff} = rac{D heta}{ au}$	Effective diffusivity	$3.34\times10^{-11}$	$m^2 s^{-1}$
$\eta \phi^2 = \frac{\text{Rate}_{\text{obs}} d_p^2}{4 V_r C_0 D_{\text{eff}}}$	Wheelr-Weisz group	$7.75\times10^{-6}$	

#### 4. Conclusions

HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> was encapsulated into the pores of HMS by in situ technique and was found to be an efficient catalyst for hydroformylation of propene. The effects of parameters: catalyst amount, Rh-complex to TEOS ratio, temperature, partial pressure of H<sub>2</sub> and CO were investigated in detail for propene hydroformylation. The conversion of propene, selectivity and iso/n ratio were found to depend on these parameters. The selectivity to n-butanal was increased on increasing the Rh-complex to TEOS ratio and partial pressure of H<sub>2</sub>. The kinetics of the Rh-HMS catalyzed hydroformylation of propene showed first order dependence with catalyst (at lower amount) and with partial pressure of H<sub>2</sub>. Substrate inhibited kinetics was observed with partial pressure of CO. The encapsulated catalyst was effectively recycled for six times without significant loss in its activity and selectivity. A study was performed for any diffusion limitations using the Carberry number and Wheeler-Weisz criterion and the reaction was found to be in the kinetic regime with negligible mass transfer limitations.

#### Acknowledgment

Authors thank Council of Scientific and Industrial Research (CSIR), New Delhi, India for the financial support through Network Project for the Development of Specialty Inorganic Materials for Diverse Applications (NWP-0010). NS acknowledge CSIR, New Delhi for the award of Senior Research Fellowship.

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