



HRh(CO)(PPh₃)₃ encapsulated mesopores of hexagonal mesoporous silica (HMS) acting as nanophase reactors for effective catalytic hydroformylation of olefins

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ABSTRACT

The rhodium complex HRhCO(PPh₃)₃ encapsulated into the pores of hexagonal mesoporous silica (HMS) by in situ synthesis (Rh–HMS) was found to be an efficient heterogeneous catalyst for the hydroformylation of C₅–C₁₂ olefins. The (Rh–HMS) catalyst system was thoroughly characterized by P-XRD, ³¹P CP-MAS NMR, FT-IR, TGA, SEM and N₂ adsorption/desorption techniques. The ³¹P CP-MAS NMR spectrum of Rh–HMS shows that the HRhCO(PPh₃)₃ complex encapsulated into the pores of HMS without decomposition, indicating that the pores of the catalyst system act as nanophase reactors. The detail investigations were performed on the effects of temperature, amount of catalyst, partial pressure of CO and H₂ and weight ratio of HRh(CO)(PPh₃)₃ to TEOS for the hydroformylation of 1-hexene. At lower temperature the selectivity and *n*/*iso* ratio of aldehydes was higher. The selectivity and *n*/*iso* ratio of aldehydes was increased on increasing the amount of HRhCO(PPh₃)₃ complex into the HMS. The catalyst had shown good thermal stability and recyclability. The catalyst was recycled giving excellent conversion (100%) for the hydroformylation of 1-hexene.

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1. Introduction

Heterogenization of transition metal complexes onto inorganic/organic supports has become one of the important research interests in catalysis [1]. Hydroformylation is one of the important reactions among the homogeneously catalyzed reactions used in industries. World production of oxo chemicals is estimated to be nearly 9.6 million metric tons in 2005; oxo chemicals find use in the manufacturing of solvents, soaps, detergents, plasticizers and various intermediates for fine and perfumery chemicals [2]. Even though homogeneous catalysts give higher conversion, selectivity and turn over frequency (TOF), these lack efficient recycling of the valuable catalyst. Compared to homogeneous catalysts, heterogeneous catalysts offer the potential advantages of easy separation and recycling of catalyst and easy purification of the products.

Different approaches such as covalent immobilization [3–9] encapsulation or adsorption of homogeneous catalyst [10–14], modification of supported metal catalyst [15–16] as well as conducting the reactions in ionic liquid [17–19] or liquid biphasic systems [20–23] have been used for heterogenization of homogeneous catalyst. Out of these only biphasic hydroformylation could

find application in industries. Other approaches have different drawbacks like low stability, selectivity, TOF and metal leaching. Therefore, investigations are needed to develop hydroformylation catalyst systems having potential properties like thermal stability, selectivity, *n*/*iso* ratio of products and reusability.

Owing to its intrinsic properties like high surface area, uniform pore sizes, acidity and thermal stability, zeolites are useful for catalytic applications in petrochemical and fine chemical industries [24]. But the limitation in pore sizes (<10 Å) made them unsuitable as a support for hydroformylation reactions [25]. This had necessitated the search for new materials with larger pores which resulted into the emergence of mesoporous materials. MCM-41, MCM-48 and SBA-15 belonging to M41S family of mesoporous silica have been extensively studied as a support for heterogeneous hydroformylation [6,7,26–28]. Other mesoporous materials have also been attempted to be used as a support to heterogenize the homogeneous catalyst. Tanev et al. have prepared a new type of mesoporous silica named hexagonal mesoporous silica (HMS) by a neutral templating route [29,30]. The neutral templates used for the synthesis of HMS are C₈ to C₁₈ amines. Dodecyl amine and hexadecyl amines are the most commonly used templates. This resembles MCM-41 with high surface area, pore volume and pore diameter but it has a specific hexagonal structure. HMS was used as a solid and robust support for reactions such as catalytic oxidation of aromatics and olefins, epoxidation of propylene, hydrodesulphurization [30–33]. Hydroformylation of olefins catalyzed by RhCl₃ anchored on Ti-HMS is reported [34]. However literature on hydroformyla-

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tion of olefins with HMS as a support is scanty. Rh/Ti-HMS/bipy catalyst system [34] has been reported for heterogeneous hydroformylation of olefins. In this catalyst system Ti-HMS was calcined in air at 650 °C for 4 h and was functionalized by 2,2' bipyridine (bipy). The functionalized Ti-HMS/bipy was used for anchoring the Rh complex. HMS can be easily synthesized at room temperature (RT). It can offer a good scope for the grafting of metal complex/organometallic moieties in to the pores to facilitate the heterogenization of homogeneous catalyst and can permit free ingress of reactants and egress of product species that have cross-sections smaller than the diameter of the pores.

In present work, a novel approach has been applied to heterogenize $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ (Rh) complex in the mesopores of HMS. The Rh-complex is anchored in situ to the organic template micelle in side the pores at room temperature. The anchoring method is elegant and does not require removing the template or functionalization of the support unlike in the case of other mesoporous [34] supports. Here, Rh-complex is encapsulated into the reverse micelle of hexadecyl amine inside the pores of HMS. Promising potential lies in the pores of Rh-HMS catalyst system to function as nanophase reactors due to the presence of micelles inside the pores. The synthesized catalyst was found to be effectively active for the hydroformylation of a wide range of olefins $\text{C}_5\text{--C}_{12}$. The catalyst has been studied in detail as a function of the temperature, concentration of the catalyst, partial pressure of the gases CO and H_2 and weight ratio of Rh-complex: Tetraethylorthosilicate (TEOS) for the hydroformylation of a representative olefin, 1-hexene.

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. The rhodium metal precursors $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, triphenylphosphine (PPh_3), sodium borohydride (NaBH_4 , 99.98%) and formaldehyde (HCHO, 34%) were purchased from Sigma-Aldrich, USA for the synthesis of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$. Tetraethylorthosilicate and liquid olefins were purchased from Sigma-Aldrich, USA. Hexadecyl amine was procured from Sisco Laboratories, India. All chemicals were used without any further purification. The double distilled milli-pore deionised water was always used during synthesis.

2.2. Synthesis of $\text{HRh}(\text{CO})(\text{PPh}_3)_3$

The metal complex $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ (Rh-complex) has been prepared by reported method [35]. A solution of rhodium metal salt, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (2.0 g, 7.6 mmol) in ethanol (70 mL) was added to a refluxing solution of triphenylphosphine, PPh_3 (12 g, 46.0 mmol) in ethanol (300 mL). After 2 min, aqueous formaldehyde, HCHO (10 mL) was added dropwise and the solution turned yellow with the formation of *trans*- $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$. Addition of sodium borohydride, NaBH_4 (2.0 g) in ethanol to the above hot mixture yielded the yellow crystals of Rh-complex. The yellow crystal was washed with ethanol to remove the unreacted rhodium metal.

2.3. Synthesis of hexagonal mesoporous silica

Hexagonal mesoporous silica was synthesized by the method reported by Tanev and Pinnavia [29]. In a typical synthesis procedure, 0.0027 mol of hexadecyl amine was dissolved in a mixture of 0.0909 mol of ethanol and 0.296 mol of deionised water. The solution was stirred at room temperature (RT) on a magnetic stirrer. To this stirring solution 0.01 mol of TEOS was added dropwise and

mixture was kept for 1 h at RT. After 1 h, the white gel precipitate formed, which was kept at RT for 18 h of aging. The material was filtered and washed with 1:1 (v/v) ethanol-water mixture and dried in vacuum at RT.

2.4. Synthesis of $\text{HRh}(\text{CO})(\text{PPh}_3)_3\text{-HMS}$

For the synthesis of $\text{HRh}(\text{CO})(\text{PPh}_3)_3\text{-HMS}$ (Rh-HMS), the in situ encapsulation of the $\text{HRh}(\text{CO})(\text{PPh}_3)_3$ into the HMS pores was done as follows. In a typical synthesis procedure, 0.0027 mol of hexadecyl amine was dissolved in a mixture of 0.0909 mol of ethanol and 0.296 mol of deionised water. The solution was stirred on 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 dropwise. 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 washed with 1:1 (v/v) ethanol-water mixture and dried in vacuum at RT.

2.5. Characterization techniques

Powder X-ray diffraction (P-XRD) patterns of the catalyst samples were recorded with Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.54050 \text{ \AA}$) over a 2θ range of $1\text{--}10^\circ$ at a step time of $0.05^\circ \text{ s}^{-1}$. ^{31}P -CPMAS NMR was recorded in a Bruker 500 Ultrashield system. The C, H and N elemental analysis of the Rh-complex was done by PerkinElmer CHNS/O 2400 analyzer. The FT-IR spectra of the samples were recorded from 400 to 4000 cm^{-1} with a PerkinElmer Spectrum GX FT-IR system using KBr pellets. Thermo gravimetric analysis (TGA) was carried out in a Mettler TGA/DTA 851e, in nitrogen flow rate at 50 mL/min. Surface morphology of samples was measured using a scanning electron micrograph (SEM) (Leo Series VP1430) equipped with EDX facility (Oxford instruments). Analysis was carried out at an accelerating voltage of 20 kV and probe current of 102 pA. The surface area analysis 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. Rh content in the catalyst was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis (Optima 2000DV, PerkinElmer instruments).

2.6. Hydroformylation of olefins using Rh-HMS

In a typical experiment, 2 g olefin dissolved in 50 mL of toluene as a solvent, with *n*-tridecane as GC internal standard was added to the 200 mg 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. The synthesis gas ($\text{CO} + \text{H}_2 = 1:1$) was charged at 40 bar. The hydroformylation reaction was then initiated by starting the stirrer at 800 rpm. The reaction was stirred for 10 h at constant temperature. After the 10 h reaction time, the reactor was cooled to RT by supplying water inside the coil. The product analysis was carried out using gas chromatography (GC) (Shimadzu 17A, Japan) and GC-MS (mass spectrometer, Shimadzu QP-2010, Japan). The GC has 5% diphenyl and 95% dimethyl siloxane universal capillary column and flame ionization detector (FID). The initial column temperature was increased from 40 to 200 °C at the rate of $10^\circ\text{C}/\text{min}$. N_2 gas was used as a carrier gas. The temperature of the 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 gas chromatography conditions. 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.

The safety precautions were always taken into utmost considerations while dealing with carbon monoxide. All the high-pressure reactions were done in a high-pressure laboratory specially made for conducting experiments at high pressure and temperature. The reactor was kept in a fume hood equipped with a strong exhaust fan. A carbon monoxide gas detector system equipped with alarm, sensing for human tolerance limit of CO, is kept in laboratory to avoid CO inhaling, in case of any leakage during handling of CO and its reaction. In addition to that, there is always a medical grade oxygen gas kept in laboratory to inhale in the case of any emergency.

3. Results and discussion

3.1. Characterization of Rh-complex

The appearance of the doublet at 53.8 and 43.4 ppm in ^{31}P -NMR spectra of Rh-complex showed that all the three phosphorous atoms possess the same environment and are in the equatorial position. The H and CO axial positions showed trigonal bipyramidal structure in the complex. The %C and %H for the Rh-complex are: calculated (found): %C = 71.9 (71.6); %H = 5.0 (5.1).

3.2. Catalyst characterization

3.2.1. Powder X-ray diffraction

The P-XRD patterns of HMS, calcined HMS and Rh-HMS are depicted in Fig. 1, which showed an intense reflection corresponding to (1 0 0) plane at 2.0° , 2.1° and 2.3° , respectively. The formation of HMS was confirmed by the peak at 2.0° , 2θ angle [29,30]. The P-XRD patterns of HMS and calcined HMS were similar and exhibited a single diffraction peak corresponding to d -spacing of 3.9 and 4.0 nm. The diffuse scattering was observed at $\sim 5^\circ$ and is attributed due to hkl reflections that are broadened as a result of small crystalline domain effects. In the case of Rh-HMS, an intense peak identical to HMS was observed. This indicated that the mesoporous phase of HMS matrix remained unaltered. The decrease in the intensity of peak in the P-XRD of encapsulated Rh-HMS is attributed to the pore filling by the Rh-complex. When the amount of Rh-complex was increased, the intensity of 100 plane got decreased due to the higher amount of Rh-complex filled inside the pore of HMS. This indicated the presence of Rh-complex

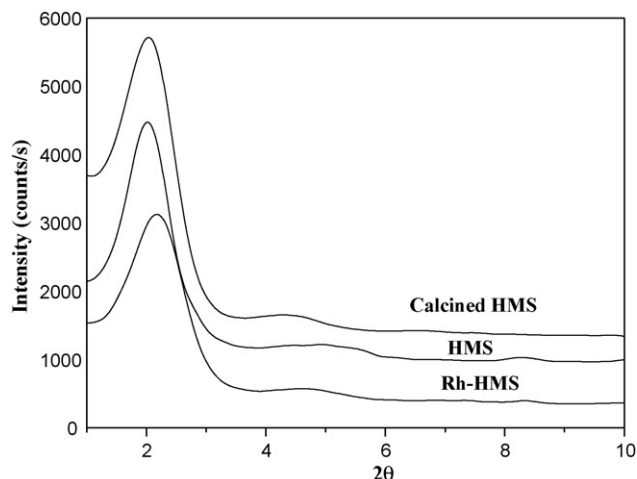


Fig. 1. P-XRD patterns of HMS, calcined HMS and Rh-HMS.

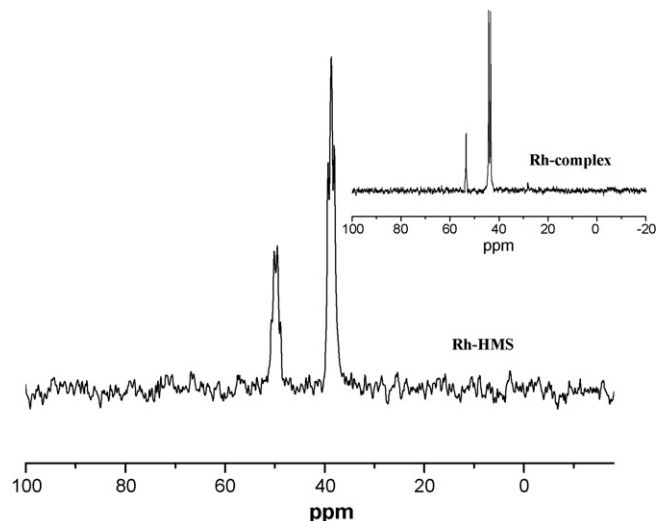


Fig. 2. ^{31}P -CPMAS NMR spectra of Rh-complex and Rh-HMS.

inside the pores of HMS. The long-range hexagonal order of weaker 1 1 0, 2 0 0 and 2 1 0 planes were not observed in the P-XRD patterns, which ensured the absence of MCM-41 type materials. This suggested that the formation of HMS was governed by weak, non-ionic interactions [36]. Materials exhibiting this single low-angle peak were considered to possess short-range hexagonal symmetry with uniform pore diameter.

3.2.2. ^{31}P CP-MAS NMR

^{31}P CP-MAS NMR spectra of Rh-complex and Rh-HMS are given in Fig. 2. The ^{31}P CP-MAS spectrum of the Rh-complex showed a doublet at 53.8 and 43.4 ppm. The ^{31}P CP-MAS NMR spectrum of Rh-HMS showed a different pattern of chemical shift ($\delta_{\text{iso}} = 50.04$, 38.70 ppm). The changes in the chemical shifts towards lower δ values indicated geometrical constraint of the complex inside the HMS pores. Also the NH_2 group of hexadecyl amine bound with the Rh-complex donates its electron pair to the Rh atom which increases the electron density on the phosphorous atoms of PPh_3 of the Rh-complex by a $(d\pi)_{\text{P}}-(d\pi)_{\text{Rh}}$ bonding [25,37]. A simple surface adsorption of complex on to the HMS should have given a chemical shift similar to that of pure Rh-complex which is not observed here [25]. These observations suggested that the Rh-complex is encapsulated in the pores of HMS and these encapsulated pores could act as nanophase reactors.

3.2.3. FT-IR spectroscopy

The FT-IR spectra of Rh-complex, HMS, calcined HMS and Rh-HMS are given in Fig. 3. The peak observed at 1072 cm^{-1} and its shoulders in FT-IR spectrum of HMS are assigned to the asymmetric stretching of Si-O-Si. The band at 798 cm^{-1} is for the internal bonds of the tetrahedral SiO_4 structural units [29]. The broad band at 3440 cm^{-1} corresponds to the hydrogen bonded surface -OH groups which were perturbed by the physically adsorbed water. The peaks at 1469, 2923 and 2854 cm^{-1} are due to the organic template present in the HMS pores. In the case of calcined HMS, all the characteristic peaks of HMS are seen, but the peaks for organic template are absent, thus indicating the removal of hexadecyl amine on calcination.

FT-IR gave further evidence for the encapsulation of Rh-complex into the HMS pores. The IR spectrum of Rh-complex encapsulated HMS had additional bands at 1919 and 693 cm^{-1} corresponding to $\nu\text{Rh-CO}$ and $\nu\text{Rh-P}$, respectively. FT-IR spectrum of the Rh-complex has these peaks at 1921 and 694 cm^{-1} , respectively [6,25]. The

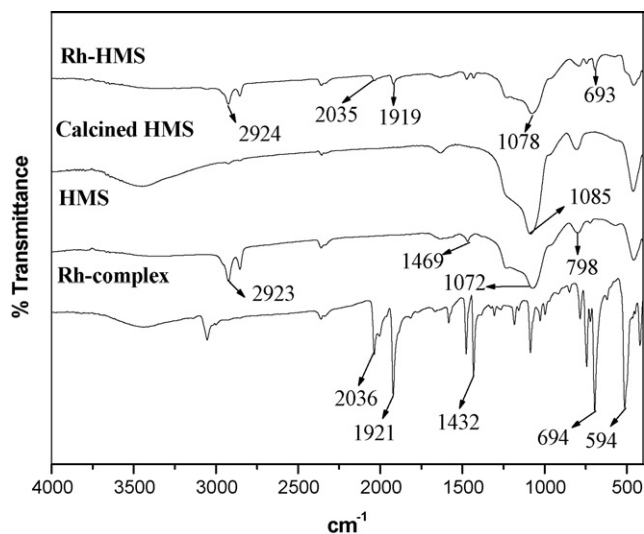


Fig. 3. FT-IR spectra of Rh-complex, HMS, calcined HMS and Rh-HMS.

shift of these bands in the case of Rh-HMS might be because of an increase in electron density on the Rh-CO and Rh-P due to NH_2 -Rh coordination arising from the interaction of hexadecyl amine and Rh-complex. The broad band at 3440 cm^{-1} is observed due to $\nu\text{Rh-NH}_2$ frequency; but the overlap of this band with that of surface silanol groups lying in the same frequency region was also found in the spectrum.

3.2.4. Thermogravimetric analysis

The TGA of hexadecyl amine, Rh-complex, HMS and Rh-HMS are shown in Fig. 4. The TGA curve gave the decomposition pattern of the organic template and the Rh-complex. The complete decomposition of hexadecyl amine was observed in the temperature range, $180\text{--}250\text{ }^\circ\text{C}$. The TGA curve of HMS showed 40% weight loss in the range of $180\text{--}280\text{ }^\circ\text{C}$. The weight loss of HMS is attributed to the loss of organic template. In the TGA plot of Rh-HMS, the catalyst showed the weight loss pattern similar to that of HMS. The weight loss of 34% in the range of $180\text{--}300\text{ }^\circ\text{C}$ is attributed to the decomposition of organic template. Another weight loss in the range of $350\text{--}450\text{ }^\circ\text{C}$ gave decomposition of Rh-complex encapsulated in the pores of HMS. Furthermore, the thermal stability of Rh-HMS was observed to increase significantly as compared to Rh-complex.

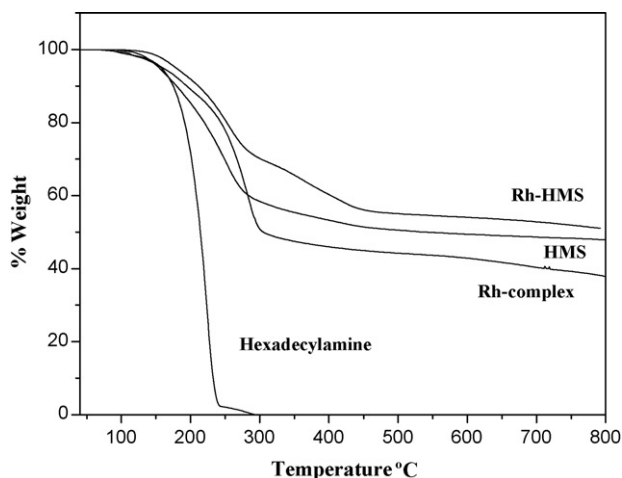


Fig. 4. TGA profiles of HMS, Rh-HMS, Rh-complex and hexadecylamine.

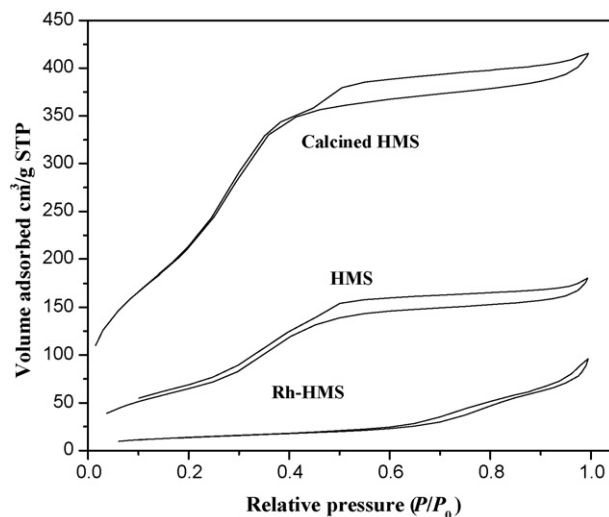


Fig. 5. Nitrogen adsorption-desorption analysis of HMS, calcined HMS and Rh-HMS.

3.2.5. Surface area measurements

Calcined HMS showed a typical Type-IV adsorption isotherm according to the IUPAC classification (Fig. 5) in the nitrogen adsorption-desorption analysis. The isotherm reveals the fact that, in case of calcined sample the surface area and pore volume being higher the volume adsorbed is higher. The increased adsorption in the P/P_0 region $0.20\text{--}0.40$ and the corresponding maxima in the pore size distribution curves (Fig. 6) indicated the existence of uniform mesopores in $2.5\text{--}3.5\text{ nm}$ size range [25]. In the case of as synthesized HMS, the reason for lower adsorption compared to calcined HMS is due to the presence of organic template inside the pores. Again in the case of Rh-HMS the volume adsorbed is very low due to the pores filling with the complex.

3.2.6. Scanning electron micrograph

The SEM images of HMS, calcined HMS, Rh-complex and Rh-HMS are shown in Fig. 7. HMS, calcined HMS and Rh-HMS showed non-uniform aggregates of very small, distinct particles. SEM image of Rh-complex showed small rod like structure. In the case of Rh-HMS, the system retained morphology similar to that of HMS, indicating that the HMS structure was not affected by encapsulation of the complex. SEM of Rh-HMS showed the absence of

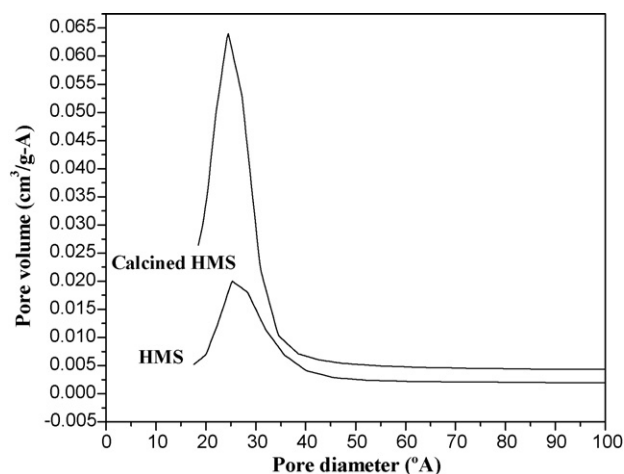


Fig. 6. Pore size distribution curve for HMS and calcined HMS.

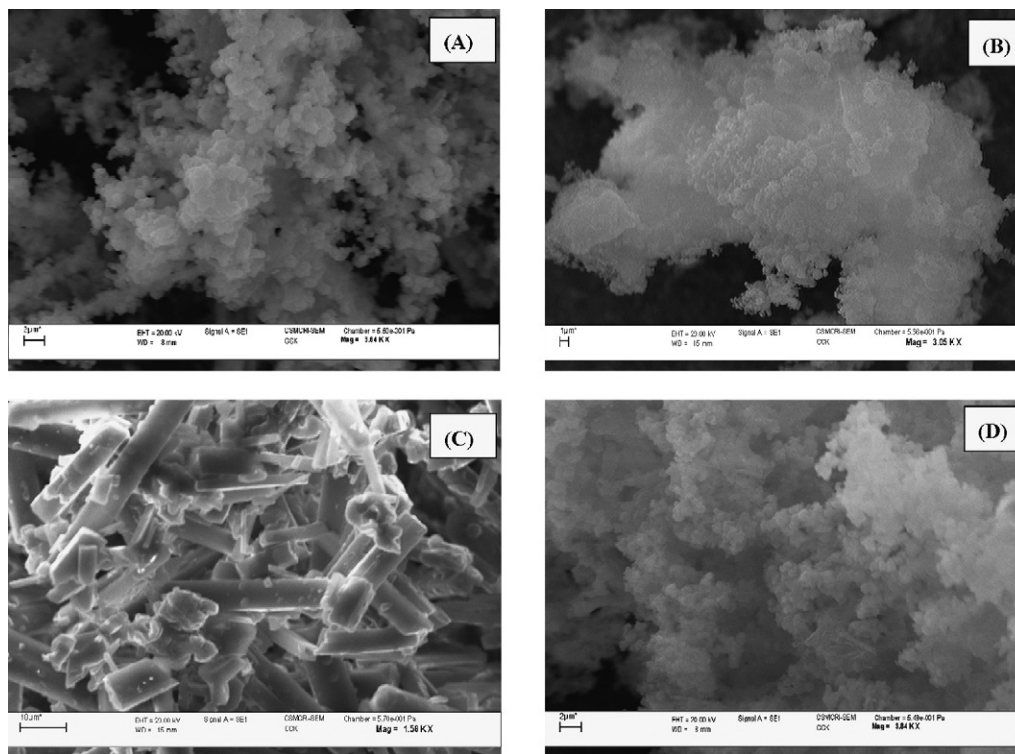


Fig. 7. SEM images of (A) HMS, (B) calcined HMS, (C) Rh-complex and (D) Rh-HMS.

Rh-complex on the surface of HMS indicating that the complex was encapsulated inside the HMS pores.

3.2.7. Inductively coupled plasma atomic emission spectroscopy

The amount of Rh content in the Rh-HMS has been determined using ICP technique. ICP analysis gave 0.6 wt% of rhodium for the Rh-HMS catalyst in which the ratio of Rh-complex: TEOS was 3 wt%.

3.3. Catalytic evaluation of Rh-HMS for hydroformylation of olefins

The Rh-HMS was evaluated as a catalyst for its activity and selectivity for hydroformylation of various olefins and the corresponding results are listed in Table 1. The conversion of olefins was observed to be >99% for all, however, the selectivity of aldehydes was found

to decrease as chain length of olefins increased. In the case of 1-hexene, 3% isomerization of 1-hexene to 2/3-hexene was observed. As the chain length of olefins increased, minor hydrogenation of olefins was also observed. All olefins gave *n*/*iso* ratio in the range of 0.7–1.0. The heterogenized catalyst showed excellent conversion and high selectivity towards aldehydes for all the olefins. The *n*/*iso* ratios of the products were relatively low in comparison to the homogeneous catalyst. The reason might be that the heterogenized catalyst has a strong isomerization activity derived from the HMS matrix, which increases the formation of iso-aldehyde [8]. The side product, ketone was formed for higher olefins. The formation of ketones in the case of ethylene and propylene were reported [36,38], but it is not so common in the case of higher olefins. In order to have a comparative insight in to the performance of Rh-HMS catalyst system, the turn over frequency for Rh-HMS

Table 1
Activity and selectivity of Rh-HMS catalyst for the hydroformylation of various olefins

Olefins	% Conversion	% Selectivity					
		<i>n</i> -Aldehyde	Iso-aldehyde	<i>n</i> / <i>iso</i> ratio	Isomerization of olefins	Hydrogenation of olefins	Other
1-Pentene	100	48	52	0.9	–	–	–
1-Hexene	100	48	49	1.0	3	–	–
1-Heptene	100	42	52	0.8	–	–	6 ^a
1-Octene	100	26	40	0.7	–	4	30 ^b
1-Nonene	100	26	37	0.7	–	4	33 ^c
1-Decene	100	30	33	0.9	–	3	34 ^d
1-Undecene	100	27	30	0.9	–	5	38 ^e
1-Dodecene	100	28	30	0.9	–	5	37 ^f

Reaction conditions: catalyst = 200 mg (Rh:TEOS = 3 wt%), olefin = 2 g, partial pressure of CO = 20 bar, partial pressure of H₂ = 20 bar, agitation speed = 800 rpm, solvent = 50 ml toluene, temperature = 80 °C, reaction time = 10 h.

^a 2-Methyl heptanone, 2-ethyl hexanal.

^b Nonanone, 2-ethyl heptanal.

^c Decanone, 2-ethyl octanal.

^d Undecanone, 2-ethyl nonanal.

^e Dodecanone, 2-ethyl decanal.

^f Tridecanone, 2-ethyl undecanal.

Table 2
Comparison of closely related catalyst systems for hydroformylation of 1-hexene

Entry	Catalyst	Rh (wt%)	Time (h)	T (°C)	% Conversion	% Selectivity of aldehyde	TOF ^a h ⁻¹	Refs.
1	Rh–HMS	0.6	1	100	89	52	1889	Present work
2	PPh ₃ –Rh/SiO ₂	1.0	0.5	100	–	83.5	1011	[13]
3	TPPTS–Rh/MCM–41	0.8	4	100	55	–	322	[17]
4	HRhCO(TPPTS)	–	0.5	100	28.7	61.3	752	[44]
5	TPPTS–Rh/SiO ₂	–	0.5	100	10.3	62.1	555	
6	HRhCO(PPh ₃) ₃	–	1.05	100	98.8	98.8	2467	[25]

^a TOF = mol aldehyde/mol Rh/h.

catalyzed hydroformylation of 1-hexene has been determined and listed in Table 2 along with closely related catalyst systems, conditions and parameters. The conversion, selectivity and TOF for the homogeneous system (Entry 6) is higher than those of heterogeneous system (Entries 1, 2, 3 and 5). Among heterogeneous catalyst systems (1, 2, 3 and 5), the conversion and TOF associated with Rh–HMS (Entry 1) are found to be higher. A comparison of biphasic catalyst system (Entry 4) indicated that the performance of Rh–HMS is better for hydroformylation of 1-hexene in terms of conversion and TOF. Also the Rh loading associated with Rh–HMS is lower (Entry 1) than that with other heterogeneous systems (Entries 2, 3), however the TOF for Rh–HMS catalyzed hydroformylation is higher.

No peak of hexadecyl amine was observed in the GC and GCMS indicating and confirming that the reverse micelles were quite stable inside the pores. The FT-IR spectra of fresh Rh–HMS and recycled Rh–HMS were recorded and given in Fig. 8. The band near 2924 cm⁻¹ has been found to be retained in the recycled Rh–HMS and intensities of the fresh and recycled catalysts were found to be almost similar. The elemental analyses of C, H were also done for fresh and recycled catalyst. The %C and %H for fresh and recycled catalyst were: %C 36.06 (35.93), %H 6.09(6.00). These findings indicated that the organic template inside the pores of HMS is stable and remained unleached during the reaction. Thus the reverse micelles formed from the organic template inside the pores were found to act as the nanophase reactor. The reaction inside occurs as that in a nanophase reactor thereby making the system more efficient for hydroformylation of higher olefins.

3.3.1. Effect of temperature on the hydroformylation of 1-hexene

In order to observe the effect of temperature on Rh–HMS catalyzed hydroformylation of olefins a series of experiments were conducted at different temperatures in the range of 50–120 °C using 1-hexene as representative olefin and the corresponding results are listed in Table 3 for 1 and 10 h reaction time. At lower time of 1 h the conversions were low (<100%) at lower temperature. On

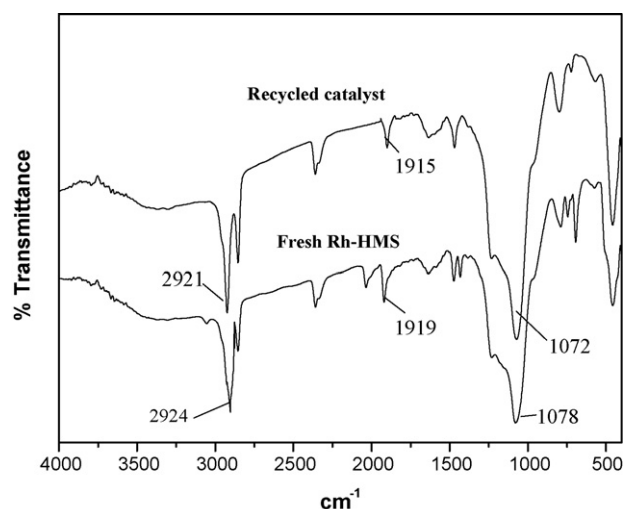


Fig. 8. FT-IR spectrum of fresh Rh–HMS and recycled Rh–HMS.

increasing the temperature from 50 to 120 °C, conversion at 1 h was increased from 65 to 95%. At the time of 10 h an excellent conversion (100%) was obtained in the entire range of temperatures. The selectivity of aldehydes being maximum, 97% at 50 °C was decreased to 81% at 120 °C. An increasing trend in isomerization was observed on increasing the reaction temperature. High reaction temperature favourable to form an isomer, in inner olefin, may be attributed for the decrease in the selectivity of aldehydes towards higher temperatures. It was observed that the *n*/*iso* ratio for the aldehyde was decreased from 1.4 to 0.8 on increasing temperature, which was also due to the increase in the isomerization of 1-hexene at elevated temperatures on HMS matrix. Based on these trends, the temperature 50 °C giving 97% aldehyde and *n*/*iso* of 1.4 was considered to be the most suitable reaction temperature for the hydroformylation over Rh–HMS catalyst. The performance of the catalyst found

Table 3
Effect of temperature on the hydroformylation of 1-hexene

Entry	Temperature (°C)	Time (h)	% Conversion	% Selectivity				
				<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> / <i>iso</i> ratio	2-Ethyl 3-methyl butanal	2/3-Hexene
1	50	1	65	32	18	1.8	–	50
		10	100	53	37	1.4	7	3
2	60	1	73	40	18	2.2	–	42
		10	100	52	36	1.4	8	4
3	70	1	84	29	16	1.8	3	52
		10	100	46	40	1.2	10	4
4	80	1	88	30	18	1.7	4	48
		10	100	44	40	1.1	13	3
5	100	1	89	30	19	1.6	3	48
		10	100	38	38	1.0	13	11
6	120	1	95	25	21	1.2	4	50
		10	100	31	38	0.8	12	19

Reaction conditions: catalyst = 100 mg (Rh:TEOS = 3 wt%), 1-hexene = 2.0 g, partial pressure of CO = 20 bar, partial pressure of H₂ = 20 bar, solvent = 50 mL toluene, time = 10 h.

Table 4
Effect of Rh-complex to TEOS ratio on the hydroformylation of 1-hexene

Entry	Rh-complex to TEOS (wt%)	% Conversion	% Selectivity					
			<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> /iso ratio	2-Ethyl 3-methyl butanal	2/3-Hexene	2-Pentyl non-2-enal
1	0.5	65	34	32	1.0	3	28	3
2	1	83	37	31	1.2	3	24	5
3	2	100	41	34	1.2	4	21	–
4	3	100	53	37	1.4	7	3	–
5	5	100	56	37	1.5	5	2	–
6	12	100	63	33	1.9	4	–	–
7	23	100	67	33	2.0	–	–	–
8	30	100	65	35	1.9	–	–	–

Reaction conditions: catalyst = 100 mg, 1-hexene = 2.0 g, partial pressure of CO = 20 bar, partial pressure of H₂ = 20 bar, solvent = 50 mL toluene, temperature = 50 °C, time = 10 h.

to be better, both in terms of conversion as well as selectivity, at low temperature (50 °C) also avoids the thermal stability issue of the catalyst.

3.3.2. Effect of Rh-complex: TEOS ratio on the hydroformylation of 1-hexene

In order to study the effect of Rh-complex: TEOS ratio on the hydroformylation of 1-hexene the Rh–HMS catalysts with different amounts of rhodium to TEOS ratio 0.5, 1, 2, 3, 5, 12, 23 and 30 wt% were prepared. The hydroformylation activities of these catalysts (Table 4) indicated that the conversion of 1-hexene increased on increasing the amount of Rh-complex. Both conversion as well as selectivity reached to 100% at the weight ratios ≥ 12 for the formation of heptanal (*n* and iso), due to the increased active sites with increased amount of rhodium. The aldehyde selectivity was also found to be increased on increasing the amount of rhodium. Catalyst with weight ratio of 3% (Entry 4) and 5% (Entry 5) exhibiting 97 and 98% selectivity for aldehydes, respectively, showed almost identical performance. 1-Hexene conversion found to be low for less rhodium loaded catalysts may be due to less active sites resulting low CO adsorption, leading to low selectivity for aldehydes.

3.3.3. Effect of the amount of Rh–HMS on the hydroformylation of 1-hexene

The effect of the amount of Rh–HMS in the wide range from 10–1000 mg was studied on the hydroformylation of 1-hexene at 50 °C and the corresponding results are listed in Table 5 for 1 and 10 h reaction time. The conversion and selectivity for the formation of *n*-heptanal were observed to increase on increasing the amount of the catalyst at 1 h time. An excellent conversion (100%) was obtained in the entire range of the varied amount of the catalyst. Even a small amount (10 mg) of the catalyst (Entry 1) was found to be significantly active. At 50 °C, isomerization was observed only

towards lower amount (10–100 mg) of the catalyst (Entries 1–3). After 400 mg amount of the catalyst, *n*/iso ratio was found to be effectively decreased. The highest selectivity of aldehydes (>98%) with *n*/iso ratio of 1.4 was observed for 100 and 200 mg of catalyst (Entries 3, 4). From 400 mg and above, aldol condensation was observed to give 2-pentyl non-2-enal. On increasing the amount of the catalyst from 400 mg and above the selectivity of *n*-heptanal was found to be significantly decreased, whereas the decrease in selectivity of iso-heptanal was insignificant. This indicated that the catalyst system has potential to be remarkably attractive for aldolization of normal aldehyde at higher amount of the catalyst. Rhodium-based catalyst supported on a solid base support is also reported for one pot synthesis of aldol derivatives from olefins [39–41].

3.3.4. Effect of partial pressure of CO on the hydroformylation of 1-hexene

The effect of partial pressure of CO on the hydroformylation of 1-hexene was studied at the catalyst amount of 100 mg (0.1 wt% of 1-hexene) and the results are tabulated in Table 6 for the reaction time of 1 and 10 h. For the 1 h time, the conversions were increased on increasing the CO pressure from 2 to 20 bar and on further increasing the pressure causes decrease in the conversion. For the higher time of 10 h, the reaction gave 97% conversion of 1-hexene with CO pressure at 2 bar and the conversion reached up to 100% at 20 bar. The selectivity of aldehyde increased on increasing CO pressure from 2–20 bars and on further increasing the pressure the selectivity of aldehyde decreased. The best selectivity obtained was at 20 bar pressure of CO (CO + H₂, 1:1) where 53% *n*-heptanal was obtained with *n*/iso ratio of 1.4. Further increase in the CO pressure, causes the formation of inactive Rh species [42] by forming di- and tri-carbonylacyl rhodium species, leading to a sharp drop in activity. At lower partial pressure of CO a positive dependence is observed,

Table 5
Effect of the amount of the Rh–HMS catalyst on the hydroformylation of 1-hexene

Entry	Catalyst amount (mg)	Time (h)	% Conversion	% Selectivity					
				<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> /iso ratio	2-Ethyl 3-methyl butanal	2/3-Hexene	2-Pentyl non-2-enal
1	10	1	16	15	16	0.9	6	63	–
		10	100	43	39	1.1	11	7	–
2	50	1	42	20	22	0.9	4	54	–
		10	100	46	38	1.2	10	6	–
3	100	1	65	32	23	1.4	–	45	–
		10	100	53	37	1.4	7	3	–
4	200	1	97	30	28	1.1	7	35	–
		10	100	56	40	1.4	4	–	–
5	400	1	98	37	30	1.2	9	24	–
		10	100	46	42	1.1	3	–	9
6	1000	1	100	36	31	1.2	3	18	12
		10	100	9	32	0.3	–	–	59

Reaction conditions: catalyst (Rh:TEOS = 3 wt%), 1-hexene = 2.0 g, partial pressure of CO = 20 bar, partial pressure of H₂ = 20 bar, solvent = 50 mL toluene, temperature = 50 °C, time = 10 h.

Table 6
Effect of partial pressure of CO on the hydroformylation of 1-hexene

Entry	CO pressure (bar)	Time (h)	% Conversion	% Selectivity				
				<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> /iso ratio	2-Ethyl 3-methyl butanal	2/3-Hexene
1	2	1	31	5	3	1.7	–	92
		10	96	21	17	1.2	–	62
2	5	1	47	13	8	1.6	–	79
		10	97	20	16	1.2	2	62
3	10	1	58	14	10	1.4	–	76
		10	100	19	16	1.2	6	59
4	20	1	65	32	23	1.4	–	45
		10	100	53	37	1.4	7	3
5	25	1	67	20	18	1.1	5	57
		10	100	48	36	1.3	4	12
6	30	1	59	19	17	1.1	5	59
		10	100	45	35	1.3	4	16

Reaction conditions: catalyst = 100 mg (Rh:TEOS = 3 wt%), 1-hexene = 2 g, partial pressure of H₂ = 20 bar, solvent = 50 mL toluene, temperature = 50 °C, time = 10 h.

Table 7
Effect of partial pressure of hydrogen on the hydroformylation of 1-hexene

Entry	Hydrogen pressure (bar)	Time (h)	% Conversion	% Selectivity				
				<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> /iso ratio	2-Ethyl 3-methyl butanal	2/3-Hexene
1	2	1	14	–	–	–	–	100
		10	32	25	15	1.7	–	60
2	5	1	18	2	2	1.0	–	96
		10	37	38	22	1.8	–	40
3	10	1	43	7	6	1.2	2	85
		10	98	38	24	1.6	–	38
4	20	1	65	32	23	1.4	–	45
		10	100	53	37	1.4	7	3
5	25	1	78	23	22	1.0	8	47
		10	100	49	38	1.3	4	9
6	30	1	93	23	23	1.0	7	47
		10	100	46	37	1.2	4	13

Reaction conditions: catalyst = 100 mg (Rh:TEOS = 3 wt%), 1-hexene = 2 g, partial pressure of CO = 20 bar, solvent = 50 mL toluene, temperature = 50 °C, time = 10 h.

pertaining to enhanced formation of active catalyst species. A similar behavior of CO pressure on the rate of hydroformylation has been reported for homogeneous [35,43] and biphasic systems [42]. On increasing the CO pressure from 2 to 30 bar the *n*/iso ratio remained to be 1.2–1.4.

3.3.5. Effect of partial pressure of H₂ on the hydroformylation of 1-hexene

The effect of partial pressure of H₂ on the hydroformylation of 1-hexene was studied by keeping constant partial pressure of CO at 20 bars at 50 °C and the corresponding results are listed in Table 7.

The conversion was very low at lower time of 1 h and at lower H₂ pressures. On increasing the pressure from 2 to 20 bar the conversion and selectivity for *n*-heptanal were increased. Further increase in H₂ pressure could not influence the conversion and selectivity. The conversion being low at 2–5 bar (35–37%), drastically changed to 98% at 10 bar at 10 h time. At 20 bar and above conversion was 100%. The formation of dimeric species shown below is reported [35] at lower pressure of H₂,

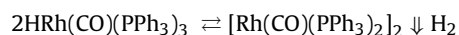


Table 8
Reusability of Rh–HMS catalyst (10 mg of catalyst)

Entry	Recycle run	Time (h)	% Conversion	% Selectivity					
				Aldehyde	<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> /iso ratio	2-Ethyl 3-methyl butanal	2/3-Hexene
1	Fresh catalyst	2	25	38	21	11	1.9	6	62
		10	100	93	43	39	1.1	11	7
2	First recycle	2	23	35	19	11	1.7	5	65
		10	100	90	40	40	1.0	10	10
3	Second recycle	2	24	34	18	12	1.5	4	66
		10	100	90	40	39	1.0	11	10
4	Third recycle	2	23	32	17	12	1.4	3	68
		10	100	89	39	38	1.0	12	11
5	Fourth recycle	2	23	28	15	10	1.5	3	72
		10	100	85	38	38	1.0	9	15

Reaction conditions: catalyst = 200 mg (Rh:TEOS = 3 wt%), 1-hexene = 2.0 g, partial pressure of CO = 20 bar, partial pressure of H₂ = 20 bar, temperature = 80 °C, solvent = 50 mL toluene, time = 10 h.

Table 9
Reusability of Rh–HMS catalyst (200 mg of catalyst)

Entry	Recycle run	% Conversion	% Selectivity					
			Aldehyde	<i>n</i> -Heptanal	Iso-heptanal	<i>n</i> /iso ratio	2-Ethyl 3-methyl butanal	2/3-Hexene
1	Fresh	100	97	47	43	1.1	7	3
2	First	100	97	40	45	0.9	12	3
3	Second	100	97	36	49	0.7	12	3
4	Third	100	96	35	49	0.7	12	4
5	Fourth	100	93	34	46	0.7	13	7
6	Fifth	100	92	31	48	0.6	13	8
7	Sixth	100	88	29	45	0.6	14	12

The formation of such species leads to a reduction in the concentration of active catalytic species at lower hydrogen pressures. The *n*/iso ratio was found to be decreased on increasing the partial pressure of H₂ which may be due to the isomerization of 1-hexene favoured by the higher H₂ environment.

3.3.6. Recycling of the catalyst for the hydroformylation of 1-hexene

The reusability of Rh–HMS for hydroformylation of 1-hexene has been studied with two different catalyst amounts of 10 and 200 mg, respectively and corresponding results are given in Tables 8 and 9, respectively. The catalyst was reused under identical conditions of the hydroformylation of 1-hexene. The recycling studies were carried out with lower amount of catalyst (10 mg) for 10 h as well as for lower time 2 h (Table 8) in which results showed 100% conversion for the fresh and recycled catalyst for 10 h. For 2 h also the conversions were not much effected and were found to be comparable for the fresh and recycled catalyst. Similar to the recycling of the catalyst amount using 10 mg, the obtained excellent conversion (100%) remained constant under the employed reaction conditions for the catalyst amount using 200 mg (Table 9) also.

The catalyst was recycled with out much decrease in selectivity. However a decrease in *n*/iso ratio of aldehydes for fresh (Entry 1, Tables 8 and 9) and recycled catalyst (Entries 2 and 3, Table 9 in case of 200 mg of catalyst) and (Entry 2, Table 8 in case of 10 mg of catalyst) occurred. It is quite possible that few Rh-complex which may be on the outer surface of the catalyst, get lost during filtration and washing processes. Decrease in *n*/iso ratio of aldehydes may be due to the loss of the Rh-complex which in turn will slightly enhance the isomerization, because the HMS having strong isomerization activity [8], remains unaffected during filtration and washing. Easy recyclability of the catalyst indicated that the catalyst is not leached out.

4. Conclusions

A rhodium complex HRh(CO)(PPh₃)₃ was encapsulated in the mesopores of HMS and was thoroughly characterized by physicochemical and spectroscopic techniques. ³¹P CP-MAS NMR characterization of the encapsulated Rh–HMS confirmed the encapsulation of HRh(CO)(PPh₃)₃ into the pores of HMS without decomposition, enabling the pores of encapsulated Rh–HMS to act as nanophase reactors. The heterogeneous Rh–HMS catalyst was found to be efficiently active for the hydroformylation of studied olefins in the range of C₅–C₁₂. The detail studies performed for a representative olefin, 1-hexene demonstrated that higher selectivity for aldehydes formation occurred at lower temperature with higher *n*/iso ratio. The hydroformylation of 1-hexene was observed to be effected by the parameters: catalyst amount, amount of complex, partial pressure of CO and H₂ and temperature. At lower temperatures the selectivity towards aldehydes was higher with higher *n*/iso ratio. The performance of the catalyst is appreciable

towards lower temperature and 50 °C was found to give best conversion (100%) and selectivity (*n*/iso = 1.4). Observation of no peak of organic template (hexadecyl amine) in the GC and GCMS analysis of product mixture and the obtained FT-IR spectra retaining characteristic organic template band with almost similar intensity for fresh and reused catalyst, indicated an excellent stability of reverse micelles and thus that of the encapsulated complex inside the pores. The catalyst was recycled at lower (10 mg) and higher (200 mg) amounts and used under identical conditions of hydroformylation of 1-hexene. The catalyst has shown good recyclability and high stability in the studied reaction conditions.

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