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Rhodium complex encapsulated functionalized hexagonal mesoporous silica for heterogeneous hydroaminomethylation

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ABSTRACT

$HRh(CO)(PPh_3)_3$ complex was encapsulated into the pores of amino functionalized hexagonal mesoporous silica. The catalyst was characterized by physico-chemical techniques like P-XRD, ^{31}P-CPMAS NMR, FT-IR, SEM, ICP and N_2 adsorption analysis. The catalyst was active for hydroaminomethylation and a variety of alkenes and amines were used as reactants for hydroaminomethylation. The catalyst afforded to achieve 100% conversion with high (>95%) selectivity to corresponding amines. Parametric variations were performed by taking 1-hexene and morpholine as representative reactants for the study of catalyst amount, temperature, pressure and 1-hexene:morpholine ratio. Significant amounts of aldehydes and enamines were observed during the course of the reaction indicating that there could be two possible rate determining steps. The catalyst was effectively recycled up to five times without much loss in its activity and selectivity.

1. Introduction

Aliphatic amines are one of the very important classes of compounds used in bulk as well as fine chemicals in the chemical and pharmaceutical industry [1,2]. Around one million tons of amines are produced annually for different uses. General methods for amine synthesis include hydrocyanation of olefins followed by reduction, reductive amination of carbonyl compounds and alkylation of organic halides with ammonia. These methods generally have drawbacks of expensive starting materials, formation of byproducts and the need of protecting and deprotecting steps involved during the synthesis. From both economic and environmental points of view, developing new versatile and direct single pot synthesis routes to amines from inexpensive and easily available feedstock is most desirable. Hydroamination [3–5] and hydroaminomethylation [6–10] are such processes for synthesis of amines with very high atom efficiency. Both these reactions have cheaper starting materials, an olefin and an amine. Hydroamination is still a very challenging reaction due to the very low TOF [11–16]. Hydroaminomethylation is a reaction that has potential to develop for industrialization.

Hydroaminomethylation (Scheme 1) is the single pot synthesis of amines from an olefin, amine (alkyl amines, morpholine, pyrollidine etc.) and syngas (H_2, CO) [17–19]. It is an elegant, atom economic, efficient process for the synthesis of amines. Hydroaminomethylation has closer applications for the synthesis of nylon, drugs and various bulk and fine chemicals.

The study of this domino reaction has undergone progress in last decade with noteworthy contributions from the research groups of Eilbracht et al. [20–23] and Beller and co-workers [24,25]. The investigations in hydroaminomethylation showed that the hydroformylation catalyst can perform equally toward hydroaminomethylation reactions by tuning the reaction conditions [17]. A variety of rhodium based catalysts have been already found to be active for hydroaminomethylation [25–32].

It is known that the homogeneous catalysts have the drawback of catalyst separation and recycling. Hydroaminomethylation currently performing in homogeneous condition also follows with the same. Hence a development of heterogeneous catalyst for hydroaminomethylation can contribute toward solving the above said problem. But the developments of catalyst system toward this route are scanty in literatures. There is a pressing need to develop catalyst system to carry out an economic, atom efficient and easily separable single pot synthesis of amines; however less attention is paid in this direction. Here we have attempted to heterogenize the well known $HRh(CO)(PPh_3)_3$ complex into the hexagonal mesoporous silica for hydroaminomethylation of olefins. $HRh(CO)(PPh_3)_3$ complex being well known for hydroformylation of olefins, its development into a heterogeneous catalyst would be an important concern. Investigation on various parameters like temperature, pressure, amount of the catalyst and olefin to amine substrate ratio are also performed.

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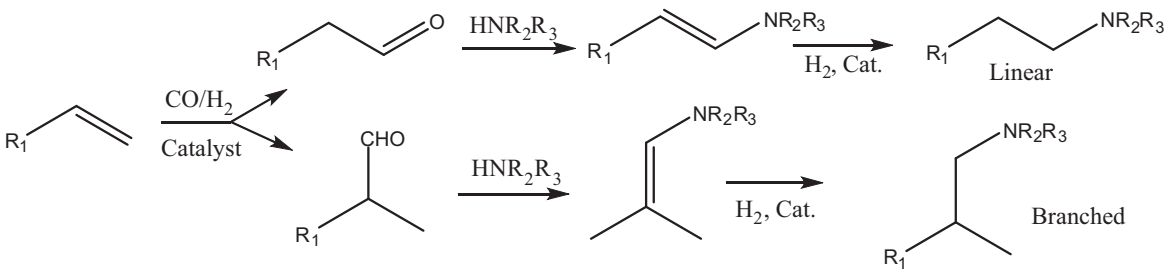


Scheme 1. Hydroaminomethylation of olefin.

2. Experimental

2.1. Materials

Tetraethyl orthosilicate, dodecylamine, aminopropyl trimethoxysilane, hydridocarbonyl tristriphenylphosphine rhodium(I) were procured from Sigma–Aldrich, USA for the synthesis of catalyst. The reactants alkenes and amines were procured from Sigma–Aldrich, USA. H_2 and CO were procured from Ami Traders, Bhavnagar, Gujarat, India.

2.2. Synthesis of the support and functionalization

Hexagonal mesoporous silica (HMS) was synthesized according to the procedure reported elsewhere [33,34]. The synthesized HMS was calcined at 650 °C for 6 h to remove the organic template and is then taken for functionalization.

The HMS has to be functionalized in order to have a good binding between the support and metal complex. In a typical synthesis procedure, 1 g of calcined HMS was taken in 15 mL of refluxing toluene and added 0.5 g of APTMS (aminopropyl trimethoxysilane). The stirring was continued for 24 h and the resultant functionalized HMS was filtered and washed with toluene and dried. The amino functionalized HMS was denoted as HMS-F.

2.3. $HRh(CO)(PPh_3)_3$ encapsulated HMS (Rh-HMS-F)

$HRh(CO)(PPh_3)_3$ (92 mg) was dissolved in 15 mL of toluene taken in a round bottom flask (RBF). This solution was placed in an oil bath set at 110 °C equipped with magnetic stirrer and RBF was connected with water condenser under nitrogen atmosphere. The functionalized HMS (1 g) was added to this refluxing solution and stirred for 24 h. The pale yellow precipitate of the heterogeneous catalyst was filtered off and dried in vacuum desiccator. The catalyst was denoted as Rh-HMS-F.

2.4. Characterization techniques

Powder X-ray diffraction (P-XRD) of the samples were recorded with Phillips X'Pert MPD system equipped with XRK 900 reaction chamber, using Ni-filtered Cu Kα radiation (λ = 1.54050 Å) over a 2θ range of 1–10° at a step time of 0.05° s^{-1}. 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. ^{31}P-CPMAS NMR was recorded in a Bruker 500 Ultrashield system. Inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Optima 2000DV, PerkinElmer instruments) was used to determine the rhodium content in the catalyst. The surface area analysis and pore size distribution of the support and catalyst were determined 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. SEM (Leo Series VP1430) equipped with EDX facility (Oxford instruments) was used for the determination of catalyst morphology. Analysis was carried out at an accelerating voltage of 20 kV and probe current of 102 pA. Thermo gravimetric analysis (TGA) was carried out using Mettler TGA/DTA 851e, in nitrogen flow rate at 50 mL/min.

2.5. Hydroaminomethylation and product analysis

Hydroaminomethylation were carried out in a 100 mL stainless steel autoclave reactor (Autoclave Engineers, USA). The experimental setup, safety precautions and procedures were similar to that described elsewhere [33]. The weighed amount of reactants (alkene and amine) and catalyst were taken in the SS-autoclave with a mixture of 30 mL of toluene and 20 mL of methanol. The autoclave was raised to desired temperature and then CO and H_2 were pressurized in the ratio required. The progress of the reaction was monitored by observing the pressure drop. Aliquots of product mixture were withdrawn to analyze the conversion and selectivity at regular time intervals. The product was analyzed by GC (Schimadzu 17A, Japan) and GC–MS (Schimadzu GCMS-QP2010, Japan). To ensure reproducibility the experiments were repeated under identical reaction conditions.

3. Results and discussions

3.1. Catalyst characterization

Low angle powder X-ray diffraction (PXRD) of calcined HMS, functionalized HMS and $HRh(CO)(PPh_3)_3$ encapsulated HMS were given in Fig. 1. These materials showed an intense reflection corresponding to 1 0 0 plane near 2θ values of 2–2.5° which corresponds to the formation of HMS [35–38]. The intensities of the peak

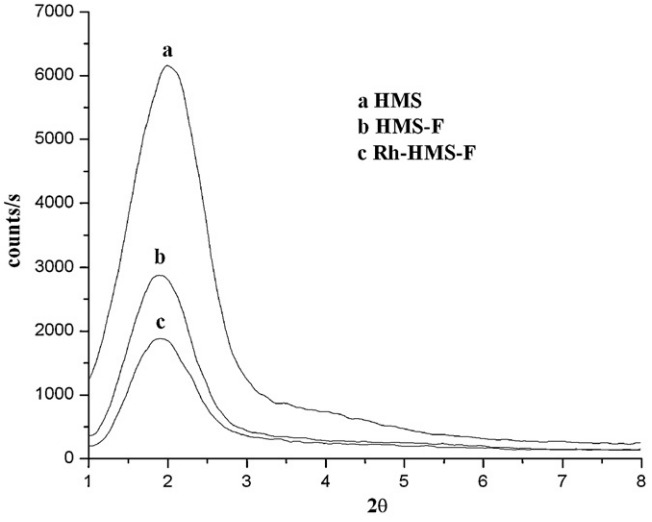


Fig. 1. PXRD of catalyst.

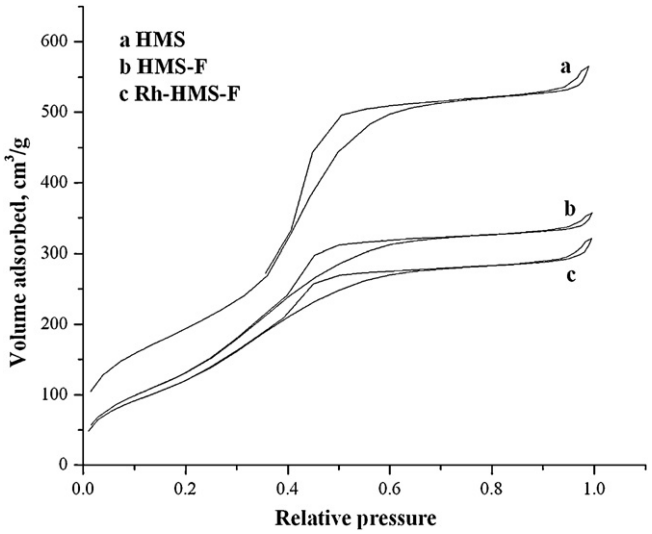


Fig. 2. N_2 adsorption isotherm.

Table 1
N_2 adsorption properties of the synthesized catalyst.

Material	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore diameter (nm)
HMS	726	0.83	3.4
HMS-F	510	0.52	3.5
Rh-HMS-F	462	0.46	3.9

were decreased on functionalization and encapsulation process. This observation is due to the pore filling by functionalization and encapsulation. There had been a shift toward lower 2θ values which is due to the expansion of pores during the encapsulation process.

The N_2 sorption analysis was done to investigate the surface area analysis of the synthesized catalysts. The sorption isotherms of the synthesized materials are given in Fig. 2. HMS, HMS-F and Rh-HMS-F showed typical Type-IV isotherm. The increased adsorption in the P/P_0 region 0.20–0.40 and the hysterises indicated the existence of uniform mesopores. The lower adsorption and decrease in the surface area and pore volume (Table 1) for the HMS-F and Rh-HMS-F was due to the pore filling occurred during functionalization and encapsulation process.

The ^{31}P-CPMAS NMR of the Rh-HMS-F was recorded and given in Fig. 3. It gave a sharp peak at 34.37 ppm corresponding to the complex inside the pores. Similar peak were observed in other reported heterogeneous catalytic systems for hydroformylation [38]. The ^{31}P-CPMAS NMR of $HRh(CO)(PPh_3)_3$ showed a peak at 43.40 ppm [33]. The shift in the position of peak from 43.40 to 34.37 ppm value may be attributed to the geometrical constraints experienced by the complex in the pores. Also the $-NH_2$ group on the functionalized HMS will get coordinated with the Rh metal center which may increase the electron density around the P atom resulting in the shift of the peak to lower ppm value [33,38].

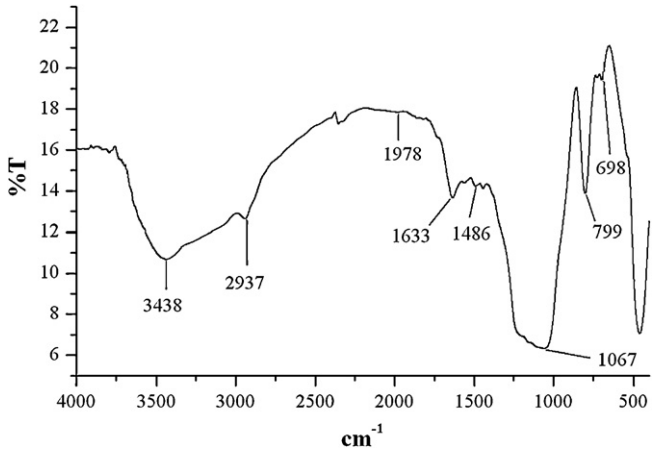


Fig. 4. FT-IR spectrum of Rh-HMS-F.

The FT-IR spectrum of Rh-HMS-F is shown in Fig. 4. The FT-IR spectrum of Rh-HMS-F showed the characteristic band at 1067 cm^{-1} for asymmetric stretching of Si—O—Si and 799 cm^{-1} for tetrahedral SiO_4 structural units. The bands at 2937 and 1486 cm^{-1} are assigned to C—H asymmetric stretching and NH_2 scissor respectively, of the functionalized APTMS present in pores. The band at 3438 cm^{-1} is corresponding to the surface —OH groups and also to the $-NH_2$ group present in the HMS matrix. The band at 1633 cm^{-1} is for the C=C stretching vibrations of the phenyl ring of the PPh_3 ligand. Rh-HMS-F showed distinguishable $\nu_{Rh\text{-}CO}$ and $\nu_{Rh\text{-}P}$ bands at 1978 cm^{-1} and 698 cm^{-1} respectively which had evidenced the encapsulation of $HRh(CO)(PPh_3)_3$ in to the pore of HMS.

The TGA analysis of the HMS-F and Rh-HMS-F is given in Fig. 5. Both of the materials showed a weight loss of ~2–4% corresponding to the adsorbed water molecules in the region of 50–120 °C. Then for HMS-F there was a weight loss of ~12% from 220 to 600 °C corresponding to the decomposition of the functionalized APTMS group. The similar kind of weight loss was observable for

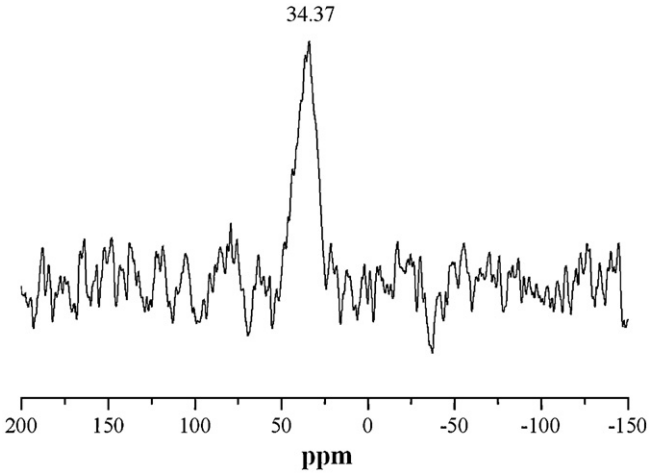


Fig. 3. ^{31}P-CPMAS NMR of the catalyst.

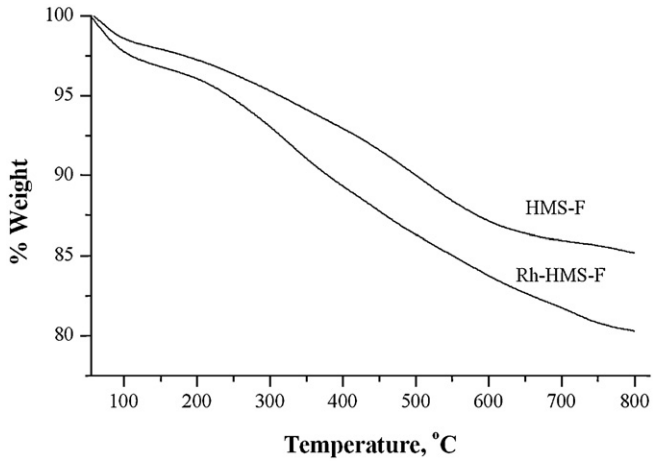


Fig. 5. TGA of HMS-F and Rh-HMS-F.

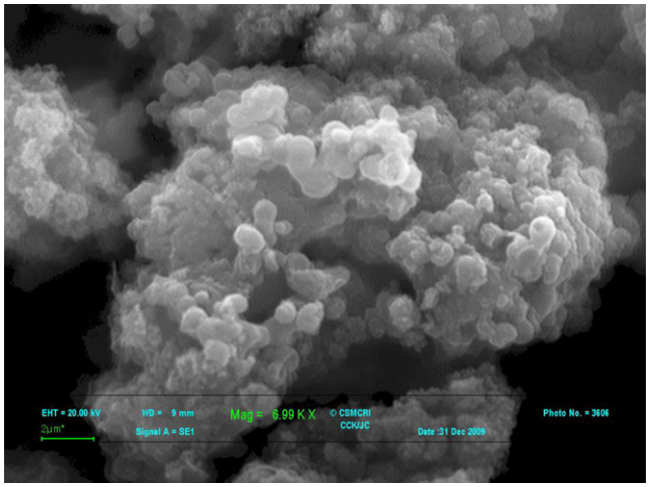


Fig. 6. SEM image of Rh-HMS-F.

Rh-HMS-F also which is ~16% corresponding to the functionalized APTMS along with the $RhCl(TPPTS)_3$ encapsulated in the HMS.

The SEM image showed the spherical nature of the catalyst which is agglomerated for the bulk (Fig. 6). Each of the spherical particles had an approximate size of 1.5–1.7 μm. The ICP analysis showed that the catalyst has 0.89 wt% of rhodium present.

3.2. Hydroaminomethylation

Hydroaminomethylation of different alkenes with different amines were carried out using the Rh-HMS-F catalyst and the results are shown in Table 2. The catalyst was active for the hydroaminomethylation of alkenes and gave 100% conversion for all the studied alkenes and amines. Amines like morpholine, pyrrolidine and piperidine were highly active by giving selectivity of >95% with small formation of enamine and N-formylated product. Reactivity of diethylamine was low toward the hydrogenation of enamine and gave 19% of enamine for 1-hexene-diethylamine hydroaminomethylation. The n/iso ratio of the products was near 1.0–1.2 in all the cases except for cyclopentene where there is no possibility of iso-product. The lower n/iso ratio depends on the regioselectivity during hydroformylation step which generally gives low value in heterogeneous conditions. A representative alkene, 1-hexene, and an amine, morpholine, were subjected for investigating the parametric effects in detail.

3.2.1. Effect of catalyst amount on hydroaminomethylation

The effect of catalyst amount on hydroaminomethylation was done by varying the catalyst amount from 25 to 100 mg and the results are tabulated in Table 3. The reaction was analyzed at two different times of 4 and 12 h to get the exact propagation of the reaction. The conversion was increased on increasing the catalyst amount from 25 to 100 mg. A conversion of 22% was obtained at 4 h for 25 mg of the catalyst (Entry 1, Table 3) which increased to 75% for 100 mg of the catalyst (Entry 4, Table 3). Conversions of 100% were obtained at 12 h for catalyst amounts of 50 mg and above. The formation of amines was low at lower catalyst amounts. Significant amounts of aldehydes were observed at both 4 and 12 h of time. Two competitive rate determining steps, formation of enamine and hydrogenation of enamine determines the rate and mechanism of hydroaminomethylation. Here the formation of enamine from aldehydes and morpholine was the crucial step which proceeded very slowly.

3.2.2. Effect of temperature on hydroaminomethylation

The effect of temperature on hydroaminomethylation of 1-hexene with morpholine was studied from 80 to 140 °C and the results are given in Table 4. The conversion was increased on increasing the reaction temperature from 25% (80 °C) to 84% (140 °C) at 4 h of reaction time. Higher selectivity was observed toward the isomerized products of 1-hexene at 4 h on increasing the temperature. The selectivity to amine gave decreasing trend at lower time on increasing the temperature which showed a reverse order on increasing the reaction time. This may be because of the increasing trend in isomerization which increases the formation of iso-aldehydes. These iso-aldehydes react slowly to form corresponding enamines and subsequently amines. The decrease in n/iso ratio also follows the same trend of decreasing on increasing the temperature. At 80 °C the reaction was very slow and the formation of amine was only 12% at 12 h of reaction time.

The reactivity of amine (morpholine) with the linear aldehyde (n-heptanal) was an easy and faster step compared to that of branched aldehyde (iso-heptanal). This facile reactivity of the n-heptanal with morpholine to linear amine was higher than that of iso-heptanal which can be observed from the higher n/iso ratio at lower time. This formation of enamine is believable to be the classical organic reaction occurring in the liquid phase and the catalyst metal center does not have significant role over this particular step [12].

Specific explanation for this reactivity difference of n- and iso-aldehydes for enamine formation is still a concern of well understanding. But the main reason ascribed for this difference is the steric hindrance around the carbonyl carbon of the aldehyde

Table 2
Hydroaminomethylation of alkenes with amines.

Alkene	Amine	% Conv.	% Selectivity				By-product
			A	B	C	D	
1-Hexene	Morpholine	100	51	0	45	3	1
1-Hexene	Hexylamine	100	42	4	46	7	0
1-Hexene	Cyclohexyl amine	100	47	0	46	7	0
1-Hexene	Pyrrolidine	100	48	1	47	2	2
1-Hexene[a]	Diethylamine	100	42	10	39	9	0
1-Hexene	Piperidine	100	49	1	47	2	1
Cyclopentene	Pyrrolidine	100	99	0	–	–	1
Cyclopentene	Morpholine	100	96	3	–	–	1
1-Pentene	Morpholine	100	53	0	44	1	2
1-Pentene	Pyrrolidine	100	52	0	47	0	1

Reaction conditions: alkene = 11.9 mmol, amine = 11.9 mmol, catalyst = 50 mg, pCO = 13.5 bar, pH_2 = 54 bar, temp. = 120 °C, toluene/methanol = 30/20 mL and time = 18 h.
By-product: N-formylated products of amine substrate.
A = n-amine, B = n-enamine/imine, C = iso-amine, D = iso-enamine/imine.
[a] 24 h.

Table 3
Effect of catalyst amount on hydroaminomethylation of 1-hexene with morpholine.

Entry	Catalyst amount (mg)	Time (h)	% Conv.	% Selectivity				
				2/3-hexene	Aldehyde	Amine	Enamine	n/iso
1	25	4	22	43	39	16	2	6.7
		12	65	21	35	36	8	4.8
2	50	4	40	27	32	38	3	4.6
		12	100	13	16	65	6	2.5
3	75	4	59	23	32	42	3	4.4
		12	100	3	21	71	5	2.6
4	100	4	75	21	28	48	3	4.5
		12	100	2	18	79	1	2.4

Reaction conditions: 1-hexene = 11.9 mmol, morpholine = 11.9 mmol, pCO = 13.5 bar, pH_2 = 54 bar, temp. = 100 °C and toluene/methanol = 30/20 mL.

[39]. Steric hindrance on the iso-aldehyde can result in low rate of formation of enamine or imine and its further hydrogenation. Therefore application of severe reaction conditions or an extended reaction time is needed to achieve higher conversions of iso-aldehyde. This is the reason for obtaining higher conversion of n-aldehyde to yield n-amine at lower reaction time. Increasing the catalyst amount also leads to the higher conversion of iso-aldehyde by increasing the hydrogenation rate of iso-enamine. Apart from steric effects, electronic effects also play a role in determining the predominant reactivity of n-aldehyde over iso-aldehyde to yield enamine or imine. Electron-donating groups (–I effect) in the carbonyl compound can decrease the rate of addition of amine with carbonyl group [39]. Branched aldehyde has higher–I effect than that of n-aldehyde leading to lower reactivity.

3.2.3. Effect of pressure on hydroaminomethylation

The effect of variation of total pressure on hydroaminomethylation is given in Table 5. The total pressure was varied from 27.5 to 83 bars by keeping the $CO:H_2$ ratio of 1:3. Both the conversion and selectivity to amine got increased on increasing the total pressure. The selectivity was higher toward the isomerized 1-hexene at lower pressures with only 34% selectivity to amines at 12 h (Entry 1, Table 5). But the lower selectivity to amines always gave higher n/iso ratio which may be due to the higher rate of enamine formation for n-aldehydes than that of iso-aldehydes in the studied conditions.

3.2.4. Effect of 1-hexene:morpholine ratio on hydroaminomethylation

The effect of 1-hexene:morpholine ratio was studied and results are given in Table 6. The conversion got decreased on increasing the ratio of morpholine. The higher concentration of morpholine may result in formation of inactive Rh-morpholine complexes which decreases the catalytic activity. The selectivity to amine also follows the same trend. Higher amount of isomerized 1-hexene were formed with increase in the morpholine ratio because of the higher isomerization rates in presence of the base, morpholine. The n/iso ratio was also decreased because of the same reason of formation of isomerized 1-hexene which in turn gives iso-aldehydes and results in higher amount of iso-enamine and iso-amine.

3.2.5. Plausible reaction steps and mechanism of hydroaminomethylation

The plausible reaction steps of hydroaminomethylation of 1-hexene with morpholine are given in Scheme 2. Firstly, 1-hexene undergoes hydroformylation to form n- heptanal (P2) and iso-heptanal (P3, 2-methyl hexanal). Here the mechanism follows the general hydroformylation mechanism. The side reaction, i.e., isomerization of 1-hexene to 2- and 3-hexene (P1) was also occurred. This formed 2- and 3-hexene can again get hydroformylated to aldehyde (n- and iso-heptanal). The conversion of 2- and 3-hexene to aldehyde increases the iso-heptanal which in turn decreases the n/iso ratio at higher reaction time. The formed aldehyde undergoes simple condensation with morpholine to form the enamine. The n-enamine formed from n-heptanal and morpholine is 4-(hept-1-en-1-yl) morpholine, P4. The iso-enamine formed from iso-heptanal and morpholine is 4- (2-methyl hex-1-en-1-yl) morpholine, P5. These n- and iso-enamines get catalytically hydrogenated over Rh active center to 4-heptylmorpholine (P6, n-amine) and 4-(2-methylhexyl) morpholine (P7, iso-amine) respectively. The n/iso ratio obtained at the initial hydroformylation stage determines the final n/iso ratio of product amines.

3.2.6. Comparison with other hydroaminomethylation systems

It is of interest to have an insight in to the performance of this catalyst system in comparison of some reported catalyzed hydroaminomethylation reactions associated with closely related reaction parameters. The most of the comparison was with homogenous systems, as to the best of our knowledge no report on heterogeneous hydroaminomethylation was found in close relation with the present investigation. It can be seen from the comparative Table 7 that the catalyst under homogenous conditions had higher reactivity in terms of lower reaction time, and regioselectivity. The biphasic hydroaminomethyaltions with water soluble ligands had lower reactivity and regioselectivity. Percentage conversions, selectivity to amine and reaction temperature associated with

Table 4
Effect of temperature on hydroaminomethylation of 1-hexene with morpholine.

Entry	Temp. (°C)	Time (h)	% Conv.	% Selectivity				
				2/3-hexene	Aldehyde	Amine	Enamine	n/iso
1	80	4	25	24	58	4	14	9.6
		12	68	32	37	12	19	5.2
2	100	4	40	27	32	38	3	4.6
		12	100	13	16	65	6	2.5
3	120	4	68	38	28	29	5	4.9
		10	100	6	17	73	4	1.8
4	140	4	84	48	26	22	4	3.2
		8	100	7	13	76	4	1.5

Reaction conditions: 1-hexene = 11.9 mmol, morpholine = 11.9 mmol, catalyst = 50 mg, pCO = 13.5 bar, pH_2 = 54 bar and toluene/methanol = 30/20 mL.

Table 5
Effect of pressure variation on hydroaminomethylation of 1-hexene with morpholine.

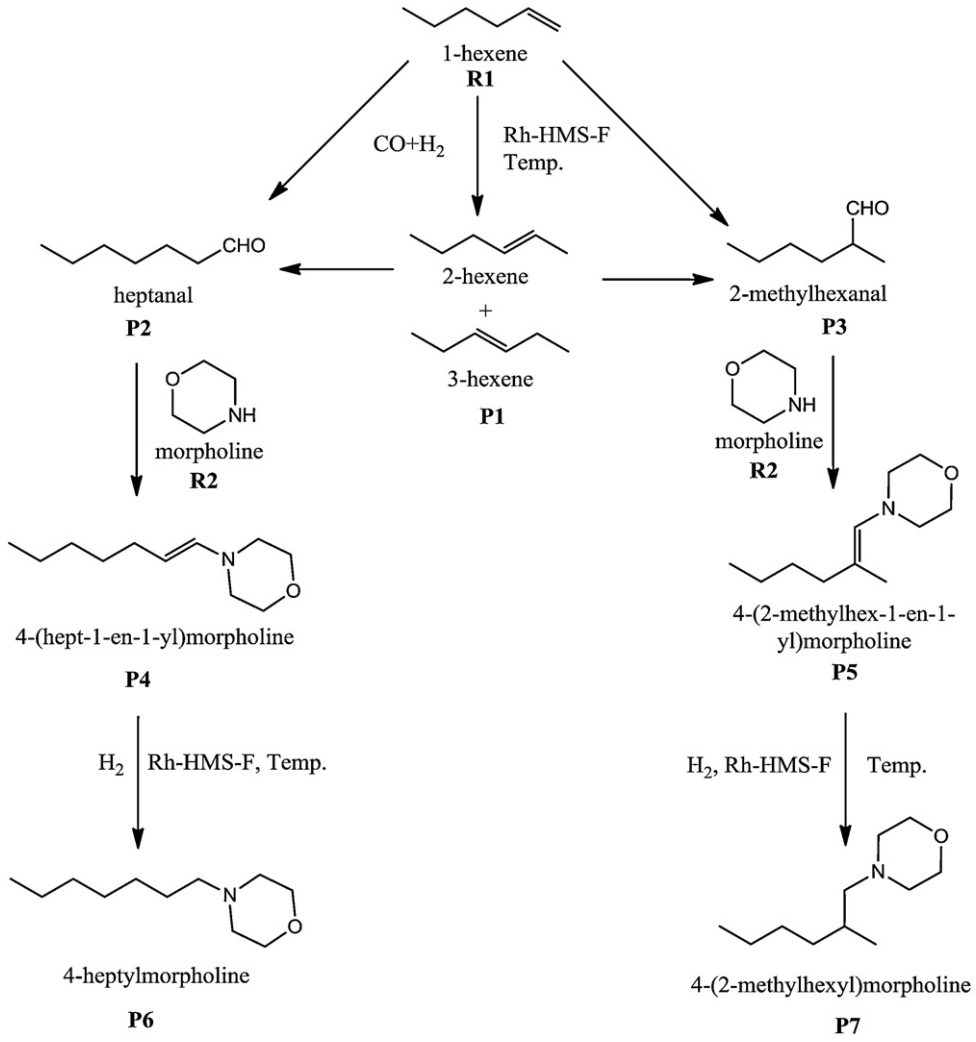
Entry	Pressure (bar)	Time (h)	% Conv.	% Selectivity				
				2/3-hexene	Aldehyde	Amine	Enamine	n/iso
1	27.5	4	28	60	29	10	1	11.5
		12	85	45	16	34	5	9.3
2	55	4	40	27	32	38	3	4.6
		12	100	13	16	65	6	3.5
3	83	4	73	26	25	45	4	4.3
		12	100	11	10	75	4	3.3

Reaction conditions: 1-hexene = 11.9 mmol, morpholine = 11.9 mmol, catalyst = 50 mg, pH_2:pCO = 4:1, temp. = 100 °C and toluene/methanol = 30/20 mL.

Table 6
Effect of ratio of 1-hexene: morpholine on hydroaminomethylation.

Entry	1-Hexene: morpholine	Time (h)	% Conv.	% Selectivity				
				2/3-hexene	Aldehyde	Amine	Enamine	n/iso
1	1:1	4	40	27	32	38	3	4.6
		12	100	13	16	65	6	2.5
2	1:2	4	34	43	23	32	2	1.5
		12	96	21	22	52	5	0.9
3	1:3	4	29	56	18	24	2	1.4
		12	82	32	24	36	8	0.85

Reaction conditions: 1-hexene = 11.9 mmol, catalyst = 50 mg, temp. = 100 °C, pCO = 13.5 bar, pH_2 = 54 bar and toluene/methanol = 30/20 mL.



Scheme 2. Plausible reactions steps for hydroaminomethylation of 1-hexene with morpholine.

Table 7
Comparison of the performance of Rh-HMS-F with some closely reported systems.

Alkene	Amine	Catalyst	Temp. (°C)	Time (h)	% Conv.	% Amine	n/iso	Ref.
1-Hexene	Morpholine	Rh-HMS-F	120	10	100	73	1.8	Present study
1-Hexene	Morpholine	Rh/BISBIS–Ionic liquid	130	5	97	86.7	11.9	[6]
1-Hexene	Morpholine	$[Rh(acac)(CO)_2]$, Tetrabi	125	6	99	99	167	[40]
1-Hexene	Piperidine	Rh-HMS-F	120	18	100	96	1.0	Present study
1-Hexene	Piperidine	$[Rh(cod)_2]BF_4$, Ionic liquid	125	17	94.1	93.4	38.3	[41]
1-Hexene	Piperidine	$[Rh(cod)_2]BF_4$, Xantphos	125	5	100	99	49.0	[17]
1-Hexene	Piperidine	$[Rh(acac)(CO)_2]$, Tetrabi	125	4	99	92.2	198.0	[40]
1-Hexene	Piperidine	$[Rh(cod)_2]BF_4$, Tetrabi	125	4	99	92.4	126	[40]
1-Pentene	Morpholine	Rh-HMS-F	120	18	100	97	1.2	Present Study
1-Pentene	Morpholine	$[Rh(cod)_2]BF_4$, Xantphos	125	5	95	99	32.3	[17]
1-Pentene	Morpholine	Rh(Imes)(cod)Cl	95	12	95	34	4.5	[42]

Table 8
Catalyst recycling.

Entry	Recycle	Time (h)	% Conv.	% Selectivity				
				2/3-hexene	Aldehyde	Amine	Enamine	n/iso
1	Fresh catalyst	4	40	27	32	38	3	4.6
		12	100	13	16	65	6	2.5
2	First recycle	4	39	30	29	36	5	4.7
		12	100	15	14	64	7	2.4
3	Second recycle	4	39	28	33	34	5	4.6
		12	100	14	16	64	6	2.4
4	Third recycle	4	37	31	31	31	7	4.8
		12	100	17	12	63	8	2.5
5	Fourth recycle	4	35	34	29	32	5	4.5
		12	100	21	15	60	4	2.3

Reaction conditions: 1-hexene = 11.9 mmol, morpholine = 11.9 mmol, catalyst = 50 mg, temp. = 100 °C, pCO = 13.5 bar, pH_2 = 54 bar and toluene/methanol = 30/20 mL.

Rh-HMS-F catalyst system are almost comparable with reported homogenous systems. However the reaction time was higher and the n/iso ratio was lower than those of homogenous systems. The promising advantage of the present catalyst is the heterogeneous nature of the reaction and the use of common Rh–PPh_3 complex.

3.2.7. Catalyst recycling

Catalyst was recycled under similar conditions by taking the catalyst from the previous cycle, which was washed with toluene and used to conduct experiments. The results of catalyst recycle are given in Table 8. The catalyst was recycled up to five cycles without much loss in its activity and selectivity. A selectivity of 65% was obtained for amine in 12 h for fresh catalyst which was dropped only to 60% in fourth cycle. The n/iso ratio was also remained almost same from 2.5 for fresh catalyst to 2.3 for fourth cycle. The reaction mixture after the reaction was analyzed by ICP for rhodium and found to be less than the detectable limit.

4. Conclusions

Aminofucntionalized HMS was used as a support for encapsulation of Rh-complex and found to be an efficient catalyst for heterogeneous hydroaminomethylation reaction. A variety of alkenes and amines were tested for hydroaminomethylation activity of the catalyst. The catalyst could give 100% conversion with a very high selectivity of >95% to hydroaminomethylation products. Enamines were found in low amounts. The catalyst was tested for parametric variations study by taking 1-hexene and morpholine as representative reactants. The parameters like catalyst amount, temperature, pressure and 1-hexene: morpholine ratio was investigated in detail. Significant amounts of aldehydes and enamines were observed during the course of the reaction indicating that there could be two possible rate determining steps, one for the formation of enamine and other for hydrogenation of enamine to amine. The catalyst was recycled effectively up to five times without much loss in its activity and selectivity.

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