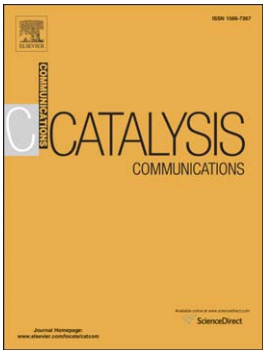

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Rhodium complexes supported on nanoporous activated carbon for selective hydroformylation of olefins

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Abstract

Activated carbon with nanoporous structure, high surface area (2500 m^2/g) and total pore volume (2.35 cm^3/g) was prepared from Mango seed shell (*Mangifera indica L.*) via chemical activation method and used as support to impregnate active hydroformylation rhodium complexes $HRhCO(PPh_3)_3$ and $Rh(acac)(CO)_2$. The prepared catalysts were characterized by XRD, SEM, TEM, NMR, IR, TGA, and N_2 adsorption/desorption techniques. The supported catalysts have shown excellent selectivity for aldehydes (~99%) in the hydroformylation of olefins with good stability and recyclability up to 4 cycles.

Keywords: Bio-wastes; Microporous-mesoporous carbon; High surface area; Hydroformylation; olefins; Rhodium.

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1. Introduction

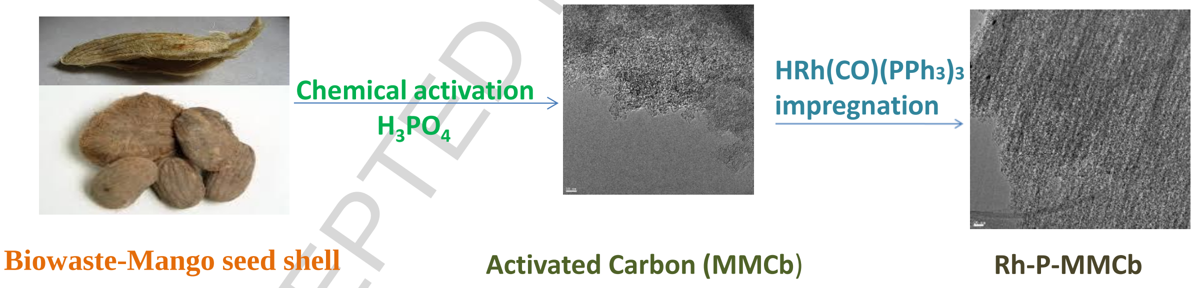
Porous carbon materials have long been commercially available as supports for precious metals like Rh, Pt, Pd and Ru for a variety of catalytic applications [1-5]. Traditional porous carbons, such as activated charcoal and carbon molecular sieves, are produced with random microporosity (pore diameter <2 nm) thereby limits the diffusion of larger reactant molecules in the pores bearing catalytically active metal particles [4]. Therefore, mesoporous carbons (MCs) with pore size of > 2 nm would be better as supports for catalytic applications. Our group has recently developed micro and mesoporous carbons from bio-waste through chemical activation method, which is amenable to large scale production of microporous-mesoporous carbons from bio-waste (**MMCb**) [6].

The **MMCb** thus developed was modified suitably to use it as support for hydroformylation catalyst for hydroformylation (HF) of olefins, which is essentially an addition reaction (100% atom efficient) of formyl group across carbon-carbon double bond to produce commercially valuable aldehydes useful in manufacturing of solvents, soaps, detergents, plasticizers and various intermediates for fine and perfumery chemicals [7]. In particular HF of 1-hexene (**Scheme S1**) using homogenous or heterogeneous catalyst is important in perfumery industry [8,9]. In heterogeneous catalytic systems, catalytic activity and selectivity are directly influenced by choice of support materials because of their textural properties (porosity and surface area) and uniqe interaction with active components. Much attention has been given to inorganic metal oxides [10-13] e.g., SiO_2, TiO_2, Al_2O_3 etc., but very few researchers have focused their efforts on carbon materials especially MCs as support for rhodium and cobalt complexes to catalyze HF reactions, [14-20] but none reported the use of **MMCb** as support.

In the present work, we have impregnated $HRh(CO)(PPh_3)_3$ and $Rh(acac)(CO)_2$ –well established hydroformylation catalysts under homogeneous condition, in **MMCb** for their heterogenization. The $HRh(CO)(PPh_3)_3$–MMCb (**Rh-P-MMCb**) and $Rh(acac)(CO)_2$-MMCb (**Rh-Ac-MMCb**) catalysts were found to be easily recyclable (4 times) and gave results (conversion, 100%; aldehyde selectivity, 99% in the case of HF of 1-hexene), which is at par with its homogeneous counterpart a la extended reaction time (12 h). These catalysts were found to be equally effective for the HF of styrene and long chain olefin 1-octene.

2. Experimental

2.1 General Remarks



Scheme 1: Synthesis of $HRh(CO)(PPh_3)_3$ –MMCb (**Rh-P-MMCb**)

Mango seeds (outer shell) were washed with distilled water and dried in an oven at 110 °C for 3 days. The dried mango seed shells (MSS, 10 g) were cut into small pieces and soaked in orthophosphoric acid (20 mL) in an alumina boat initially at 110 °C for 24 h then at 400 °C for 2 h to produce activated carbon. The black hard solid mass was removed from the reactor and washed with distilled water to remove traces of orthophosphoric acid. The wet-mass thus obtained was dried at 110 °C for 8 h in oven and named as **MMCb**. For the synthesis of $HRh(CO)(PPh_3)_3$–MMCb (**Rh-P-MMCb**), 1.0 g of **MMCb** was added to a solution of HRh(CO)(PPh_3)$_3$ (100 mg) in toluene (20 mL) under nitrogen atmosphere and the resulting slurry was stirred for 18 h at room temperature. Subsequently, the solvent was removed under reduced pressure and the resulting mass was dried at 120 °C overnight in an oven under nitrogen. (**Scheme 1**)The same procedure was followed for the preparation of catalyst **Rh-Ac-MMCb**.

3. Results and discussions

The XRD (**Fig.1**) patterns of **MMCb**, **Rh-P-MMCb** and **Rh-Ac-MMCb** have shown a very broad peak suggesting amorphous nature of these materials.

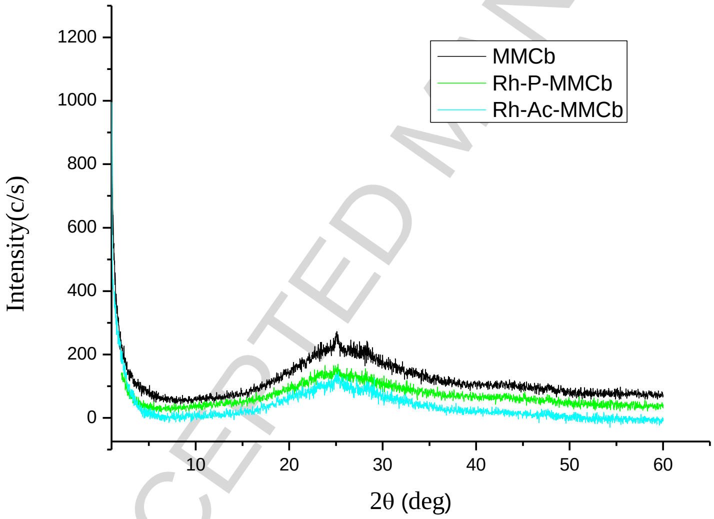
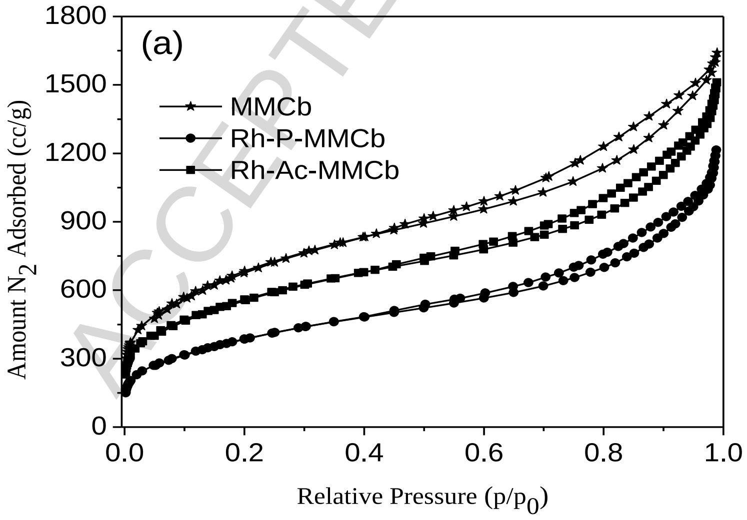


Fig. 1 PXRD patterns of **MMCb**, **Rh-P-MMCb** and **Rh-Ac-MMCb**.

The TGA of **MMCb**, **Rh-P-MMCb** & **Rh-Ac-MMCb** under nitrogen atmosphere are shown in **Fig. S1** (see supporting information). All the samples were dried under vacuum at 110 °C for 4-6 h before the TGA measurements. In the case of **MMCb** there was a gradual weight loss of nearly 18.62% was observed possibly due the slow decomposition carbon as carbon dioxide. Whereas, in the case of catalysts **Rh-P-MMCb** & **Rh-Ac-MMCb** a loss of 27.13 and 27.37% respectively were observed due to the decomposition of respective complexes impregnated in the carbon matrix.

The N_2 adsorption-desorption isotherms (at 77 K) of **MMCb**, **Rh-P-MMCb** and **Rh-Ac-MMCb** and their corresponding Density Functional Theory (DFT) pore size distribution (PSD) curves are shown in **Fig. 2** (a) and 2 (b). All the isotherms can be classified as composition of type-I and type-IV isotherms according to IUPAC indicating the presence of micro- and mesopores. The higher uptake of N_2 at low relative pressure ($p/p_0<0.2$) is mainly due to the presence of micropores. The samples show H3 type of hysteresis, which is associated with aggregated or plate like particles thereby forming slit shaped mesopores. The nature of isotherms and hysteresis loop remained unchanged even after Rh-complex loadings, except that there was some reduction in N_2 adsorption capacity. As prepared activated carbon (**MMCb**) is having high surface area (2500 m^2/g) and total pore volume (2.35 cc/g) (Table S1), which reduces on impregnation of Rh-complexes (**Rh-P-MMCb** & **Rh-Ac-MMCb**) thereby, confirming their effective loading on porous carbon.



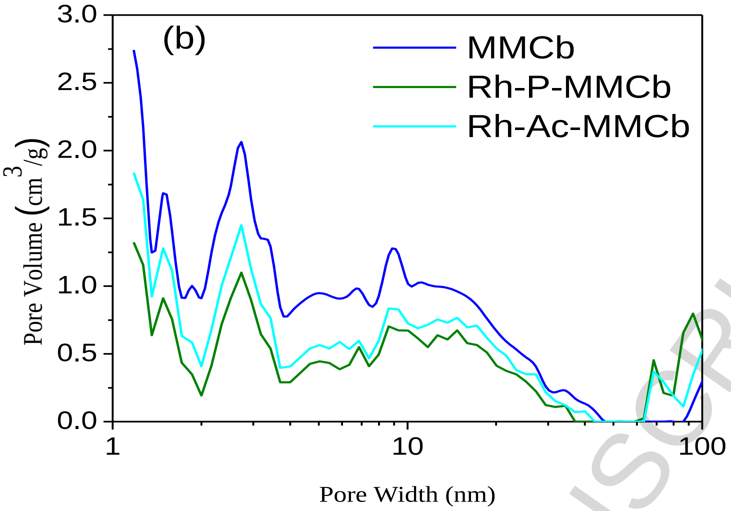


Fig. 2 (a) Nitrogen adsorption-desorption isotherms at 77 K and (b) DFT-pore size distribution curves of **MMCb**, **Rh-P-MMCb**, **Rh-Ac-MMCb**.

The ^{31}P CP-MAS (**Fig. 3**) spectrum of the $HRh(CO)(PPh_3)_3$ showed well defined characteristic doublet at 57.6 and 46.5 ppm [21] and expected these peaks in **Rh-P-MMCb** get broadened and appear at 58.7 and 43.8 ppm respectively indicating successful impregnation of active complex on the carbon support. A similar behaviour has been reported earlier in the case of herterogenization of $HRh(CO)(PPh_3)_3$ on silica support [22].

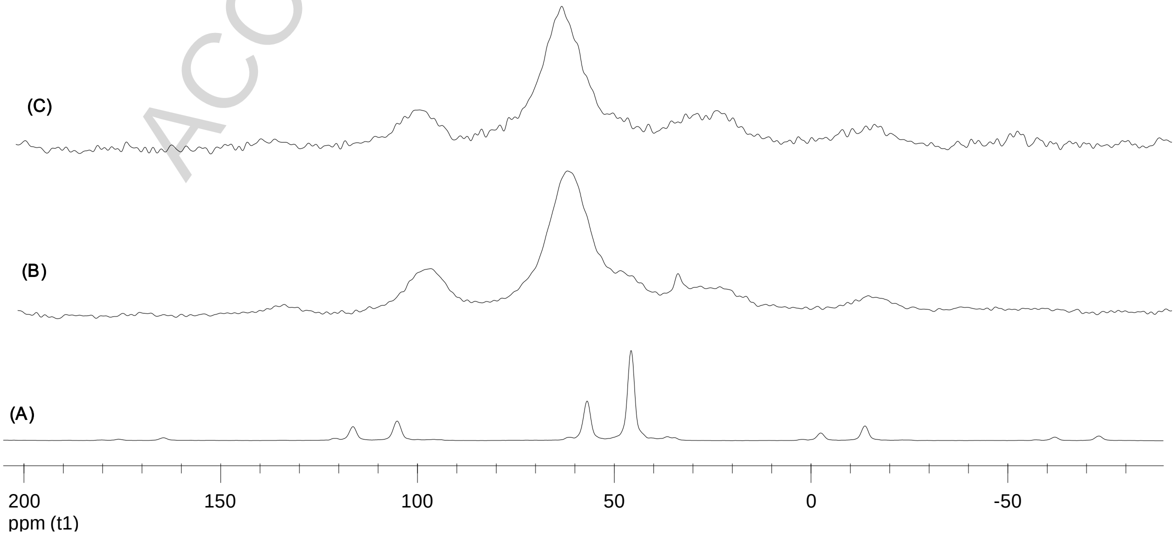


Fig. 3 ^{31}PNMR Spectra of $H(Rh)(CO)(PPh_3)_3$., **Rh-P-MMCb** and **(C)** Re used **Rh-P-MMCb**

The SEM images of **MMCb** (**Fig. S2a**) and **Rh-P-MMCb** (**Fig. S2b**) non-uniform aggregates of very small, distinct particles. The textural property of **MMCb** was not changed on supporting $HRh(CO)(PPh_3)_3$ to get **Rh-P-MMCb** indicating that the texture of carbon support is robust.

The TEM image (**Fig. 4**) and elemental mapping (**Fig. S2c**) of the **Rh-P-MMCb** showing microporous-mesoporous structure with fairly uniform distribution of metal complex. ICP together with elemental analysis showed that the **Rh-P-MMCb** contains 0.6 wt% of Rhodium.

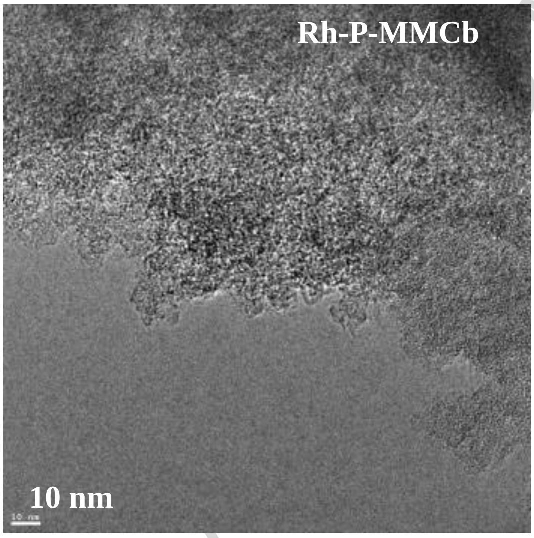


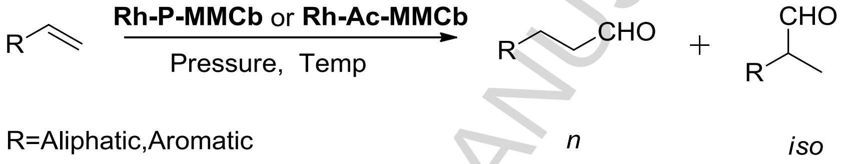
Fig. 4 TEM image of **Rh-P-MMCb**.

FT-IR spectrum **Fig. S3** of **MMCb** is typical of amorphous carbon rich in C=C bonds (broad band at 1618 cm^{-1}), however on impregnation of $HRh(CO)(PPh_3)_3$, bands typical to virgin complexes centered around 3431 cm^{-1}, 1618 cm^{-1}, 1147 cm^{-1}, 504 cm^{-1} and additional bands at 1919cm^{-1} and 693 cm^{-1} corresponding to υRh-CO and υRh-P respectively. In both cases there were no changes observed in the IR spectra of reused catalysts clearly show that these complexes are firmly secured on **MMCB**.

3.1. Catalytic performance of the Rh catalysts

It has been reported that Rh-complexes supported on activated carbon are active catalysts for the HF of olefins to give corresponding aldehydes in excellent yields [2,19,20,23]. Therefore, **Rh-P-MMCb** was evaluated as catalyst for its activity and selectivity for the hydroformylation of 1-hexene as model substrate with syngas ($CO+H_2$) at 3-7 MPa pressure and 60-120 °C temperature and the results are listed in **Table 1**. At first we varied pressure over 1-7 MPa (**Table 1**, entries1-4) keeping the reaction temperature constant at 60 °C and found that 7 MPa pressure has given 100% 1-hexene conversion with corresponding product aldehyde having n/iso ratio of 1.4. Hence, for subsequent variation in reaction conditions we took 7 MPa pressure as constant and varied temperature. Increasing temperature from 60 to 80 °C (**Table 1**, entries 4-5) caused slight decrease in n/iso ratio of the product with no change in conversion, however a further increase in temperature not only affect product selectivity but also cause isomerization of 1-hexene and in turn produce *iso*-aldehydes (**Table S2**). The selectivity of aldehyde in hydroformylation is mainly affected by isomerization of alkene, which is temperature dependent. At lower temperatures (60-80 °C), the isomerization of alkene is lower and consequently the higher aldehydes selectivity can be realized. The isomerization of alkene produces the internal alkenes which are difficult to hydroformylated at low syngas pressure. Therefore, in the case of low syngas pressure unreacted internal olefins remained in the system causing overall lower aldehyde selectivity. At comparative higher syngas pressure, internal alkenes are converted into aldehydes and therefore isomerization products of alkenes are found to decrease with an increase of syngas pressure [9,13]. It is to be noted that at the optimized reaction condition, virgin **MMCb** neither produce any product nor causes isomerization of olefin (**Table1**, entry 8), indicating that the support is benign and do not by itself contribute to the product formation. Under the optimized condition the hydroformylation of 1-hexene using **Rh-Ac-MMCb** as catalyst affected 100% products formation with n/iso ratio of 1.3 (**Table 1**, entry 9, which is slightly inferior as compared to its **Rh-P-MMCb**. The catalytic performance of **Rh-P-MMCb** is also compared with homogeneous Rh-complex at similar metal loading and reaction condition. The **Rh-P-MMCb** showed comparable aldehyde selectivity to its homogenous counterpart although require higher reaction time to get complete conversion of 1-hexene (**Table 1**, entry 10).

Table 1 Activity and selectivity of **Rh-P-MMCb** catalyst for the hydroformylation of Olefins



Entry	Pressure MPa	Temp. (°C)	Conversion (%)	Selectivity (%)			
				n-ald.	*iso*-ald.	n/i	Isomerization
1	1.0	60	40	42	36	1.1	22
2	3.0	60	55	51	37	1.3	12
3	5.0	60	85	53	39	1.3	08
4	7.0	60	100	58	42	1.4	-
5	7.0	80	100	56	44	1.3	-
6	7.0	100	100	49	50.3	1.0	0.7
7	7.0	120	100	51.4	48	1.0	0.6
8[a]	7.0	60	-	-	-	-	-
9[b]	7.0	60	100	53	47	1.3	-
10[c]	7.0	60	100	61	37	1.9	2
11[d]	7.0	60	100	48	52	0.9	-
12[e]	7.0	60	100	23	77	3.3	-

Reaction conditions: catalyst-**Rh-P-MMCb** = 25 mg, 1-hexene = 1.0 g, pressure of CO/H_2 = 7MPa (1:1), toluene = 50 mL, time = 12 h. [a]**MMCb** (25 mg) as catalyst, [b]catalyst-**Rh-Ac-MMCb**., [c] $HRh(CO)(PPh_3)_3$ as catalyst with reaction time = 5 h, [d] substrate: 1-octene,

[e] substrate: styrene.

The activity and selectivity of **Rh-P-MMCb** was further checked for the hydroformylation reaction of 1-octene and styrene (**Table1**, entries 11 and 12). In the case of 1-octene iso product formation was more (**Table1**, entry 11 n/iso ratio 0.9) than what was obtained with 1-hexene and this ratio was even greater in the case of styrene (**Table1**, entry 12, n/iso ratio 3.3). In order to compare the performance of **Rh-P-MMCb** and **Rh-Ac-MMCb** catalysts, the results of the closely related known catalytic systems are listed in **Table S3**. It is evident from the comparison that the catalysts **Rh-P-MMCb** and **Rh-Ac-MMCb** have matching performance notwithstanding the advantage of using easily synthesized support from bio-waste. In conclusion both **Rh-P-MMCb** and **Rh-Ac-MMCb** were found to be effective olefin hydroformylation catalyst to give corresponding aldehydes exclusively but with moderate n/iso ratios.

It is know that the catalyst activity of impregnated catalyst is also depend on type of support used and its porous structure. Therefore, we compared the efficacy of the **MMCb** support, $H(Rh)(CO)(PPh_3)_3$ impregnated on various other supports viz., commercially available activated carbon, silica, acidic alumina, zirconia, and ZnO in the hydroformylation of 1-hexene under similar reaction conditions. The data depicted in (**Fig. S4**) show that **Rh-P-MMCb** catalyst had fared better than others notwithstanding the utilization of bio-waste in the preparation of support used in the present study. **Rh-P-MMCB** catalyst has high specific surface area and porous structure with wide range of nanopores. Due to these properties of support, the higher dispersion of catalyst was observed and the substrate molecules can easily approach to active metal center without diffusion limitation. In turn, the remarkable catalyst activity can be realized with **Rh-P-MMCB** in comparison to other supports.

Reusability (4 times at 60 °C) of the catalyst **Rh-P-MMCb** studied in the hydroformylation of 1-hexene under the optimized reaction conditions (**Fig. S5**) showed no considerable change in conversion and selectivity over the studied cycles. Noticeably, the ICP analysis of the organic phase obtained after first cycle showed ~3% of the rhodium leaching, but this Rh-loss has not significantly affected the performance of the recycled catalyst. In subsequent cycles however, the ICP analysis of the solution phase showed no trace (if at all below detection level) of Rh metal.

4. Conclusions

MMCb having high surface area of 2500 m^2/g and pore volume (2.35 cm^3/g) synthesized from waste biomass was used to support complexes $HRh(CO)(PPh_3)_3$ and $Rh(acac)(CO)_2$. The as-synthesized heterogeneous catalysts are recyclable and showed excellent activity and aldehyde selectivity with moderate *n/iso* ratio in the hydroformylation olefins.

Acknowledgments

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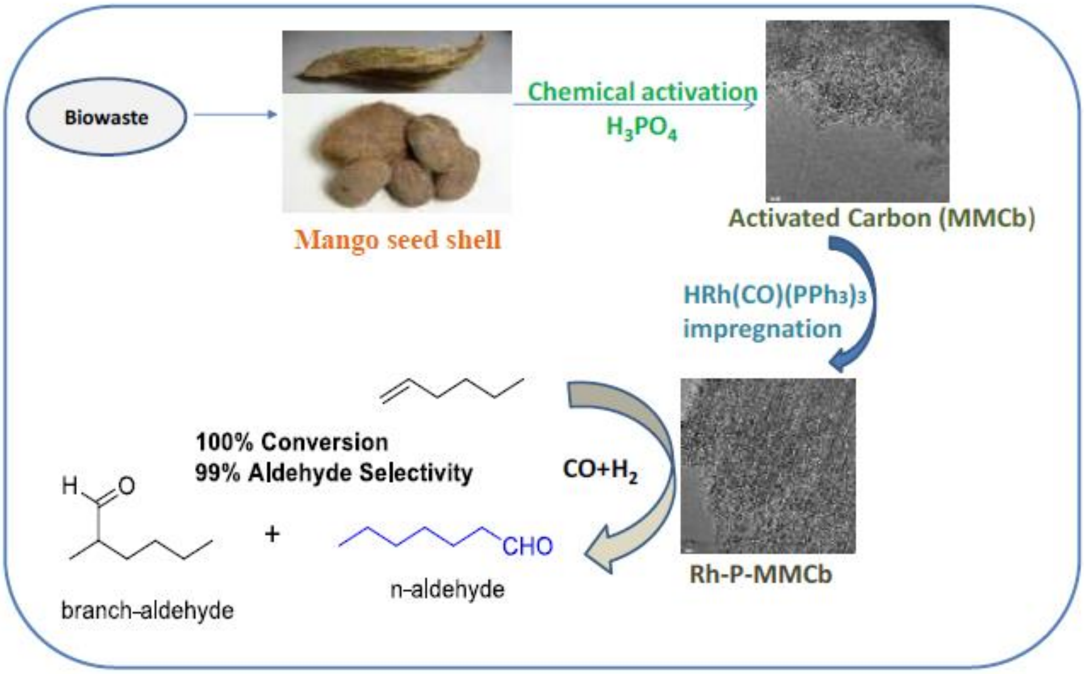

Graphical abstract

Highlights:

- Nanoporous activated carbon derived from Mango seed shell used as support
- Rhodium complexes were heterogenized on nanoporous activated carbon
- Selective hydroformylation of olefins was investigated using supported Rh catalyst
- Supported Rh catalyst showed high selectivity towards aldehyde up to 99%
- Supported Rh catalyst was found to be stable over several recycle run