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Carboxylic Group Embedded Carbon Balls as a New Supported Catalyst for Hydrogen Economic Reactions

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Carboxylic group functionalized carbon balls have been successfully synthesized by using a facile synthesis method and well characterized with different characterization techniques such as XPS, MAS NMR, SEM, ICP and N₂ physi-sorption analysis. The synthesized material has been effectively utilized as novel support to immobilized ruthenium catalyst for hydrogen economic reactions.

Keywords: Carbon Balls, Immobilisation, Metal Complex, Transfer Hydrogenation.

1. INTRODUCTION

Hydrogen is gaining growing significance as a future energy carrier due to the depletion of the world oil reserves in the coming decades. This will lead to shortage of H_2 as feedstock for chemical processes such as synthesis of ammonia, methanol and higher alcohols from aldehydes and ketones, which currently comprises nearly 50% of the total H_2 amount produced on an annual basis. This calls for novel strategies which limit H_2 usage in the chemical sector, particularly in hydrogenation reactions.

Immobilized catalysts are of interest not only to sustain a clean environment but also are of commercial relevance through efficient separation and subsequent recycling.^{1,2} Various industrial catalysts consists of metals or metal compounds supported on an appropriate support, the basic role of which is to maintain the catalytically active phase in a highly dispersed state.4,5 Solid carbonaceous materials carried much attention in recent years in the field of catalysis in both liquid phase as well as vapour phase reaction either as catalyst or as a support due to their exceptional properties like high pore surface area, relatively inert and ability to sustain in high pressure and temperature conditions. Current technologies develop various new fascinating carbonaceous materials for specific tasks.⁵ However, it is difficult to introduce a functional group onto the carbon material due to its hydrophobic nature and chemical inertness.^{6–9} If carbon materials possesses functional groups during its synthesis and consequently, to provide anchoring sites for metal complexes, they can serve as an excellent support for the preparation of metal complex immobilized catalyst. Out of innumerable metal complexes ruthenium phosphine

complexes are commercially important because of their high applicability in industrial hydrogenations as homogeneous catalysts.^{10, 11} Although homogeneous catalysts in general have a higher activity than supported catalysts, they may not be recovered easily, which may increase costs and lead to metal pollution in water.¹

Catalytic hydrogenations are important class of chemical transformations for the synthesis of fine as well as bulk chemicals. From an environmental and economical point of view the transfer hydrogenation (MPV reduction, Meerwein–Pondorf–Verley) represents a convincing route for their synthesis because of its high atom efficiency and safety advantages.^{12–17} Here, the report consists of a novel carboxylic group functionalized carbon immobilized ruthenium catalyst for MPV reduction.

The main objective in this study was to achieve covalent anchoring of $(RuCl_2(PPh_3)_3)$ complex to carbon support through carboxylic groups in lowest number of steps. For the covalent anchoring of $(RuCl_2(PPh_3)_3)$, we attempted to use in-situ synthesized carboxy functionalized material. The use of this carboxy functionalized material in covalent anchoring of metal complex is reported here for the first time. The catalyst system was characterized for their physicochemical properties by different techniques to establish their integrity and stability for use as heterogeneous catalysts. The efficiency of the catalyst system was assessed in the MPV reduction of cyclohexanone and the reaction conditions were optimized to get higher substrate conversions. To generalize the methodology different substrates were tested under optimized reaction conditions.

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2. EXPERIMENTAL SECTION

2.1. Chemicals

All the solvents and chemicals were purchased from Aldrich Chemicals and used as received.

2.2. Catalyst Characterizations

Ruthenium content in the catalyst materials were estimated by inductively coupled plasma atomic emission spectrometry (ICP-AES). The prepared carbon materials were characterized by N₂ physisorption measurements at 77 K using an Autosorb 1C setup (Quantachrome) adsorption analyzer. Prior to the measurements, the samples were degassed under vacuum $(1 \times 10^{-5} \text{ Torr})$ for 2 h at 200 °C. The BET specific surface areas were determined from the adsorption data in the relative pressure (P/P_0) range from 0.06 to 0.2. Morphology of the materials synthesised were investigated using SEM (FEI Quanta 3D). X-ray photoelectron spectroscopy (XPS) measurements were carried out in an ultra-high vacuum (UHV) setup equipped with a monochromatic Al K α X-ray source $(h\nu = 1486.6 \text{ eV})$, operated at 14.5 kV and 35 mA, and a high resolution Gammadata-Scienta SES 2002 analyzer. The base pressure in the measurement chamber was maintained at about 7×10^{-10} mbar. The measurements were carried out in the fixed transmission mode with pass energy of 200 eV, resulting in an overall energy resolution of 0.25 eV. A flood gun was applied to compensate the charging effects. Resolution spectra for C 1s, O 1s, and N 1s were recorded. The binding energy scales were re-calibrated based on the sp² hybridized C 1s line from graphitic carbon at 284.5 eV. The Casa XPS softwareⁱ with a 70:30 Gaussian-Lorentzian product function and Shirley background subtraction was used for peak deconvolution. The obtained spectra from different elements were plotted using the same intensity scale for all the analyzed samples to facilitate comparison.

Solid state (¹³C) cross polarization magic angle spinning (CPMAS) NMR spectra were recorded using DSX 400 WB Brucker spectrometer operating at 9.39 GT. The sealed sample was sent into a zirconia rotor (\emptyset 4 mm). ¹H (399.94 MHz), ¹³C (100.56 MHz) MAS spectra were recorded using cross polarization pulse program. The measurements were carried out at 298 K with the MAS rate of 10 kHz. ³¹P MAS NMR spectrum of the catalyst was recorded using a using DSX 400 WB Brucker spectrometer. The chemical shifts were measured taking 85% H₃PO₄ as the reference.

2.3. Catalyst Synthesis 2.3.1. Synthesis of -COOH-Functionalized Carbon Nanospheres

D-glucose monohydrate (21 g) was dissolved in water (107 ml) in Teflon-lined autoclave. Acrylic acid monomer was then added to the solution (10% wt with respect to the glucose amount). The reaction mixture was then sealed



Figure 1. SEM micrographs of Ru/catalyst.

in the autoclave and maintained at 160 °C for 20 h. The obtained products (6.0 g) were isolated by filtration and washed with ample amount of water.¹⁹

2.3.2. Ionic Exchange of -COOH-Functionalized Carbon

The COOH-functionalized carbonaceous material was suspended in 100 ml of deionized water. pH was adjusted at



Figure 2. C XP spectra of Ru/catalyst.

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Figure 3. ¹³C MAS NMR of Ru/catalyst (left) and ³¹P NMR of (inset) neat ruthenium complex, Ru/catalyst (right).

8 by using 1 M KOH solution and further ion-exchanged with potassium nitrate. The solution was stirred for 24 h before filtration. The obtained material was dried at 100 $^{\circ}$ C under vacuum.

2.3.3. Immobilization of Ruthenium Complex (RuCl₂(PPh₃)₃)

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 $RuCl_2(PPh_3)_3$ (0.05 g) dissolved in 50 ml of dichloromethane was slowly added to 1 g of the cation exanged carbonaceous materials, and the mixture was stirred at room temperature overnight. The resulting solid was filtered, washed repeatedly with dichloromethane, and then dried under vacuum at 40 °C to get the Ruthenium complex covalently anchored onto carbon (hereafter Ru/Carbon).

2.3.4. Determination of COOH Group in Carbon by Chemical Analysis

The determination of –COOH group in carbon balls was carried out by the conventional chemical analysis, i.e., the ion-exchange method using calcium acetate.¹⁹ Carbon (ca. 0.5 g), which had been pretreated with 1.0 M HCl for 24 h, was precisely weighed and placed in a 100 ml flask together with 50 ml of 0.2 M calcium acetate solution. The flask was shaken under room temperature for 10 days. After filtration, the filtrate was titrated with a 0.1 M NaOH standard solution using phenolphthalein as an indicator. A blank titration also has been made solution without carbon.

2.3.5. Catalyst Testing

In a typical reaction, substrate (10 mmol), Ru/Carbon (100 mg, 0.005 mmol of Ruthenium from ICP analysis), 0.01 g KOH and 100 mmol of 2-propanol were placed in a were placed in a round bottom flask (batch reactor) fitted with reflux condenser, equipped with a magnetic stirrer

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and immersed in a thermostatic oil bath for maintaining the desired reaction temperature. The reactions was conducted at the desired temperature and the progress of the reaction was monitored by withdrawing reaction mixture samples periodically, centrifuged and analyzed for their compositions a Agilent gas chromatograph with a capillary column (cross-linked methyl silicone gum, HP1, 50 m \times 0.2 mm i.d.) and a flame ionization detector (FID). The product identification was achieved by using standards and GCMS (Agilent). 2016 10:07:40

3. RESULTS AND DISCUSSION

The specific surface area of the catalyst system was found to be 20 m² g⁻¹. Figure 1 shows the morphologies of the catalyst; it is observed that the surface of the particles is not smooth and particles assemble into micrometer-sized "raspberry"-like structures. To confirm the presence of carboxylic groups in the material after and before immobilization of metal complex we applied XPS to check the functionality; The XPC 1s spectra of Ru/COOH are shown in Figure 2. The spectra were deconvoluted into 5 components. The two main peaks at 284.5 and 285.6 eV were assigned to sp² hybridized graphite-like carbon (C–C sp²) and sp³ hybridized diamond-like carbon (C–C sp²). The peaks centered at 287.1 and 288.8 eV were attributed to surface oxygen groups assigned as –C=O and –COO.



Scheme 1. Cyclohexanone to Cyclohexanol.

Substrate	Products	Conversion (mol%)	TON^b	Selectivity (%)
Cyclohexanone ^c	Cyclohexanol	65	1300	99
Cyclohexanone	Cyclohexanol	63	1260	99
Cyclohexanone ^d	Cyclohexanol	99	990	99
Cyclopentanone	Cyclopentanol	61	1220	99
Cyclohexene-1-one	Cyclohexene-1-ol	39	780	99
Acetophenone	Phenylmethanol	56	1120	99
Benzophenone	Diphenylmethanol	51	1020	99
Benzaldehyde	Benzyl alcohol	53	1060	99
Bromo Benzaldehyde	Benzyl alcohol	58	1160	99
Chloro Benzaldehyde	Benzyl alcohol	60	1200	99
Cinnamaldehyde	Cinnamyl alcohol	47	940	99
Crotonaldehyde	Crotonyl alcohol	49	980	99
1,4-Benzoquinone	1,4-dihydroxybenzene	62	1240	99

Table I.	MPV	reduction	of	various	substrates	over	Ru/carbon	catalyst ^a .
THOIC TO	1111 1	reaction	01	various	Substrates	0,01	rtu/cui oon	culuiyot .

Notes: ^{*a*}Reaction conditions: 10 mmol of the substrate, 2-propanol 100 mmol, temperature 85 °C, time 12 h, substrate to catalyst molar ratio = 2000:1; ^{*b*}TON (turn over number) mole substrate converted per mole of Ru; ^{*c*}The reaction was carried out under homogeneous condition with neat metal complex, which was completed within 12 h; ^{*d*}The substrate to catalyst molar ratio taken was 1000:1.

Additional features occurring at 291.7 eV is attributed to the satellite of sp² graphite-like carbon.¹⁸ After immobilization of metal complex we applied solid-state ¹³C CP-MAS NMR to ensure the functionality and immobilisation (Fig. 3). The ¹³C spectra of as synthesized carboxy functionalized carbon and metal complex immobilized carbon possesses almost similar pattern. The large peak between 5 and 90 ppm¹⁹ indicates the presence of aliphatic and ether carbons, the presence of peaks between 100 and 170 ppm because of sp²-hybridized carbons, the peak at 180¹⁹ is observed because of carboxylic acids plus a low amount of aldehydic groups, while in the 210 ppm region ketones and a small population of aldehydes resonates.¹⁹ The determination of -COOH group in functionalized carbon sample was carried out by the conventional chemical analysis, i.e., the ion-exchange method using calcium acetate.²⁰ The content of -COOH group in the sample is found to be 5 mmol/g (theoretical value); experimental value (4.2 mmol/g). MAS NMR is a good technique for investigating ligand fictionalization and complex anchored onto the support. Because the Ru/Carbon samples contained small amounts of phosphorus, we used cross-polarization $(^{1}H-^{31}P)$ MAS NMR to enhance the sensitivity of the ^{31}P signal. The ¹H-³¹P coupled CP-MAS NMR spectra of the neat Ru complex and Ru/Carbon are depicted in Figure 3. The ³¹P peak corresponding to Ru/Carbon exhibits a shift at δ 29 ppm, compared with that of neat Ru complex at

Table II. MPV reduction of cyclohexanone with different secondary $alcohols^{a}$.

Alcohols	Conversion (mol%)	Selectivity (%)	
2-propanol	63	99	
2-butanol	65	99	
2-pentanol	62	99	
Cyclopentanol	60	99	
Cyclohexanol	61	99	

Note: "Reaction conditions: 10 mmol of the substrate, Sec-alcohol = 100 mmol, temperature 85 °C, time 12 h, substrate to catalyst molar ratio = 2000:1.

 δ 29.1 ppm, possibly due to the different environments.²¹ ³¹P NMR studies clearly revels that the Ru complex is covalently anchored to the carbon support.

The efficiency of the ruthenium immobilized catalysts prepared was assessed in the MPV reduction of cvclohexanone (Scheme 1) and other substrates. These results are summarized in Table I. Cyclohexanone was chosen as the test substrate, and the heterogeneous MPV liquid-phase MPV reduction was carried out with a substrate to catalyst molar ratio of 2000:1 in isopropanol at 85 °C. A homogeneous liquid phase reaction was also performed with neat ruthenium complex under similar conditions for comparative purpose. It was found that the activity of heterogeneous system was comparable with neat complex in homogeneous system. The results presented in Table I clearly demonstrate that cyclohexanone was MPV reduction with conversion (up to 63%) and 99% selectivity of cyclohexanol which are comparable with the homogeneous analogue (entry 2, Table I). decreasing the substrate-to-catalyst molar ratio from 2000 to 1000 caused significant increase in the conversion of cycloxenone, but did produce a decrease in the selectivity of cyclohexanol (Table I, entries 7 and 8). Consequently, the ruthenium complex with a single step immobilised to carboxy functionalized carbon are active catalysts for MPV reductions-a significant and important finding of our studies.

 Table III. MPV reduction of various alkyl cyclohexanones with

 2-propanol over Ru/catalyst^a.

Substrate	Conversion (mol%)	cis/trans	
Cyclohexanone	63	_	
2-methylcyclohexanone	60	32:68	
3-methylcyclohexanone	60	28:72	
4-methylcyclohexanone	61	15:85	

Note: ^{*a*} Reaction conditions: 10 mmol of the substrate, 2-propanol = 100 mmol, temperature 85 °C, time 12 h, substrate to catalyst molar ratio = 2000:1.

Table IV. Effect of molar ratio of cyclohexanone and 2-propanol in MPV reduction^{*a*}.

Cyclohexanone to sec-alcohol molar ratio	Conversion of cyclohexanone (mol %)		
1:5	54		
1:10	63		
1:20	49		
1:40	37		

Note: ^aReaction conditions: 10 mmol of the substrate, temperature 85 °C, time 12 h, substrate to catalyst molar ratio = 2000:1.

A series of secondary alcohols have been applied to evaluate the effect of molecular structure of alcohol for the MPV reduction of cyclohexanone using Ru/carbon catalyst. Table II demonstrates that all the alcohols studied are reactive, 2-propanol and 2-butanol gave the best activities and selectivities for the MPV reaction. There was no significant difference observed in case of secondary alcohols like 2-pentanol, cyclopentanol and cyclohexanol as reported in the literature due to negligible diffusional constrains in the present catalyst system.^{22, 23}

To study the effect of different substrates we applied substituted cyclohexanones. Interestingly, there was very little differences observed of these substrates which could be due to absence of ring induced steric hindrance of the substrates towards the active species.²⁴ Moreover, in the case of all the above-mentioned ring substituted cyclic ketones, selectivity towards the trans product is found to be higher than the cis isomer and the *transicis* ratio is depicted in Table III.

The effect of molar ratio between the substrate and hydrogen donor, in the MPV reduction of cyclohexanone using 2-propanol with Ru/Carbon catalyst also has been studied (Table IV). It was observed that higher the amount of 2-propanol the lesser was the conversion and maximum conversion was obtained at a ratio of 1:10 between cyclohexanone and 2-propanol. A possible explanation is that either the excess amount of alcohol may interfere in the coordination of substrate with the metal sites and thereby retard the polarization of the carbonyl group of the substrate or lower contact time of substrates and catalyst.²² However, below 1:10 molar ratios the conversion is less and at 1:5 ratio may be due to high viscosity of the reaction mixture.

The effect of reaction time over substrate conversion in the MPV reduction of cyclohexanone is illustrated in Figure 4(a). The figure showed that substrate conversion increased as a function of time and reaching optimum conversion in 12 h for Ru/Carbon.

We used the various catalysts to study the effect of temperature (range, 55–95 °C) in the MPV reduction of cyclohexanone. The results indicate that a temperature of 85 °C is required to acquire the activation energy for hydrogenation for the immobilized catalyst system. At this temperature, the maximum conversion of cyclohexanone (up to 63%) was obtained by all of the catalyst systems under the reaction conditions studied. Raising the temperature above 85 °C produced no further change in substrate conversion for the catalyst, as shown in Figure 4(b).

In addition to alkyl-substituted cyclohexanones, a variety of other aldehydes and ketones were also applied to establish the current methodology over Ru/carbon with 2-propanol as reducing agent (Table I). Cyclohexanone is more readily reduced than cyclopentanone. Conjugation between the carbonyl bond and the C=C double bond in 2-cyclohexene-1-one makes these compounds more difficult to reduce than saturated ketones. Acetophenone slowed down the reduction compared to cyclohexanone. Substituents in the aromatic ring have an effect on the conversion and selectivity of the reaction due to inductive and resonance effects. The incorporation of an electronwithdrawing group with lone pair electrons such as Cl, Br in the benzene ring resulted in an enhanced rate of reaction compared to the unsubstituted aldehyde. Similarly, complex aldehydes such as crotonaldehyde and cinnamyl aldehyde reduced to alcohols without reduction of



Figure 4. (a) Effect of time on stream in MPV reduction of cyclohexanone over Ru/carbon catalyst (b) Effect of temperature in MPV reduction of cyclohexanone over Ru/carbon.

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Table V. Evaluation of leaching and recyclability of Ru/carbon catalyst for MPV reduction^a.

Ru	content	TON^b	Selectivity (%)	
Fresh	0.05 mmol/g	1260	99	
1st cycle	nd	1240	99	
2nd cycle	nd	1240	99	
3rd cycle	nd	1200	99	
4th cycle	nd	1200	99	

Notes: ^aReaction conditions: 10 mmol of the substrate, 2-propanol 100 mmol, temperature 85 °C, time 12 h, substrate to catalyst molar ratio = 2000:1: ^b TON (turn over number) mole substrate converted per mole of Ru.

carbon-carbon double bonds which reinforces selectivity of the current methodology.

3.1. Catalyst Stability

To investigate whether any active species of the catalyst were leaching into the reaction medium, we carried out MPV reduction of cyclohexanone under selected conditions with Ru/Carbon catalyst. The reaction was stopped after 3 h, after which the reaction was cooled to room temperature and conversion of cvclohexanone was estimated. Then the catalyst was separated by hot filtration, the filtrate was added to the vessel, and the reaction was continued for another 10 h. No increase in substrate conversion was observed; it remained the active species of the catalyst into the reaction mixture; the catalyst truly acted as if it were heterogeneous. This observation confirms the complete absence of leaching of any active species in reaction Sole DIA. Annis and E. N. Jacobsen, J. Am. Chem. Soc. 121, 4147 medium.

We evaluated the recyclability of the Ru/Carbon catalyst in the MPV reduction of cyclohexanone in four runs; the results are presented in Table V. After each run, the catalyst was washed repeatedly with dichloromethane, dried under vacuum at 40 °C for 6 h, and then used in the MPV reduction with a fresh reaction mixture. Cyclohexanone conversion was practically almost same (63%) in all four recycles, with a marginal decrease at the third and fourth cycles. This could be due to mechanical loss of catalyst during regeneration. This finding demonstrates the successful immobilization of the Ruthenium complex onto the novel carbon support.

4. CONCLUSIONS

The report demonstrated a new, effective class of heterogeneous catalyst through synthesis of ruthenium complex covalently anchored carboxylic functionalized carbon in least steps. Catalyst diagnosis demonstrated the successful incorporation of carboxylic groups and metal complex onto the carbon material. The catalyst system was found to be the ideal heterogeneous catalyst system for the MPV

reduction of ketones and aldehydes. The reactivity study of ketones, aldehydes and alcohols with different molecular structure showed that the approach can be applicable for wide verity of substrates. The high catalytic activity of Ru/Carbon for the MPV reaction can be attributed to the higher dispersibility of ruthenium complex in the support. The catalyst was reused for four recycles, with same activity and selectivity. Thus, we consider this protocol to be a readily accessible pathway to highly immobilized transfer hydrogenation catalyst.

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