

FULL PAPER

WILEY-VCH

Ru@PsIL Catalysed synthesis of N-formamides and benzimidazole using Carbon Dioxide and Dimethylamine Borane

Vitthal B. Saptal,^[a] Takehiko Sasaki ^[b] and Bhalchandra M Bhanage*^[a]

Abstract: This work reports the synthesis and characterization of ruthenium nanoparticles (Ru NPs) supported on polymeric ionic liquids (PILs). This catalyst shows high catalytic activity towards the N-formylation of amines and synthesis of benzimidazoles from 1,2 diamines and carbon dioxide (CO2) by reductive dehydrogenation of dimethylamine borane. This methodology shows excellent functional group tolerance with broad substrate scope towards the synthesis of N-formamides and benzimidazoles. Interestingly, this protocol also provides the tandem reduction of 2-nitroamines and CO₂ to synthesize benzimidazoles. It was proposed that the ionic liquid phase of polymer plays pivotal roles such as assisting the stabilization of nanoparticles electrostatically, providing the ionic environment and controlling the easy access of the substrates/reagents to the active sites. The developed methodology utilizes the CO₂ as C1 source and water: ethanol as green solvents system. Additionally, the catalyst was found to recyclable in nature and shows five consecutive recycle runs without significant loss in its activity.

Introduction

The high emission of greenhouse gas (CO₂) is considered as the biggest environmental issue, due to its negative impact on nature. In 2014 about 36 Gt anthropogenic CO₂ was emitted, which corresponds to the 9.8 Gt of carbon.^[1] Consequently, the transformation of CO2 to value-added chemicals have attracted intense interest.^[2-3] The use of CO₂ is considered as the greener, sustainable and economical C1 source than other C1 sources not only due to the easy to handling and low cost but also due to its renewable and environmentally friendly nature.^[2] However, due to the high stability of CO₂, the activation and subsequent transformation of the activated form of CO2 to value-added chemicals is highly challenging and demanding from the industrial as well as academic perspectives.^[3] Among the various reactions reported for the transformations of CO2, the reductive functionalization of amines with CO₂ has developed as a highly sustainable approach that provides the most valuable products.^{[4-} 61

In the recent year, the use metal nanoparticles (NPs) in the field of catalysis is highly demanding due to their high reactivity, good

[a] V. B. Saptal, Prof. B. M. Bhanage
Department of Chemistry, Institute of Chemical Technology
Matunga, Mumbai-400 019 (India)
Fax: (+91) 22-33611020
E-mail: bm.bhanage@gmail.com
[b] Prof. T. Sasaki
Department of Complexity Science and Engineering
Graduate School of Frontier Sciences
The University of Tokyo
5-1-5, Kashiwanoha, Kashiwa, Chiba 277-8561 (Japan)

Supporting information for this article is given via a link at the end of the document. recyclability and outstanding selectivity.^[7] In this regards, the stabilization of NPs and designing of their architectures and functionalities is an important task, which mostly depends on the selection of the right ligands on the surface of NPs, comprised of diverse coordinating elements and pendant moieties.^[8-10] It has been observed that the specific performance of these nanomaterial's for certain applications mostly depends on the synthesis and stabilization techniques employed, suggesting the importance of coordinating linkers on NP surfaces.^[11]

The utilization of ionic liquids (ILs) for vast applications and in many diverse fields such as chemistry, materials science and specific catalysis have been witnessed over last few years.^[12] Further, the immobilization of ILs onto various supports has been succeeded in order to stabilize the metal NPs that can be used for various applications.^[13-15] The ILs are well-known as a suitable media for the synthesis of NPs, leading to a proper stabilization of NPs by interaction with the ILs molecules.^[16-20] In this context, the polymeric materials having functionalities analogous to ILs (polymeric ionic liquids: PILs) have been followed for the development of innovative classes of cutting-edge materials.^[21-22] The presence of functional moieties having ionic nature in the polymer backbone enhances the dispersion and stabilization of NPs. Also, the immobilized ILs as supports for catalysts, not only take benefit of excellent physicochemical properties of ILs but also helps in increasing the recyclability of catalysts and easy the catalyst-product separation.^[23-31] The immobilization of ILs on polymer acts like a solid support and provide the similar electronic environment like ILs for the stabilization of NPs.[31]

In continuation of our research interest towards the catalytic fixation of CO₂.^[54-57] herein, we have synthesized and characterized the Ru NPs (Ru@PsIL) stabilized onto the supported ionic liquid phase. These as-synthesized NPs applied as a multitasking catalyst for the synthesis of formamides, benzimidazoles and one pot reduction and cyclization of nitroaniline to benzimidazoles under the mild conditions (scheme 1). In addition, the high catalytic activity and good recyclability observed for the Ru@PsIL have emphasized the utility of the protocol employed.

Results and Discussion

The typical synthetic procedure for preparation of Ru@PsIL is shown in scheme 2. This synthesized catalyst is characterized by using various analytical techniques. The SEM images of Ru@PsIL clearly show the good dispersion of the ruthenium NPs over the spherical and wrinkled polymer support (Figure 1a). The well-oriented spheres clearly show the stabilization of the Ru NPs on the SILP (Figure 1b). The closer view of the catalyst also shows the wrinkled surface of the support where well stabilized NPs can be visualized (Figure 1c, 1d).

FULL PAPER







Figure 1 SEM images of Ru@PsIL (a) and (b) showing the spherical morphology with the wrinkled surface of Ru@PsIL, (b) and (c) shows the well stabilized Ru NPs onto the wrinkled surface of the PsIL.

The catalyst was also characterized by using the X-ray photoelectron spectroscopy (XPS). The XPS survey scan spectrum of Ru@PsIL reveals the presence of all expected elements like Ru, C, N and O (ESI, Figure S-2). In the overall XPS survey, the overlapping of peaks around at 285 eV of C 1s and Ru 3d brings the difficulties in assigning the spectrums for C and Ru elements, the 3p of Ru was chosen for the analysis. The metallic state of Ru is characterized by Ru 3p3/2 peak at ~462.3 eV and Ru 3p1/2 peak at ~464.5 eV while the Ru (IV) is characterized by two peaks at ~463.7 eV and ~486.2 eV respectively.^[69] The synthesized Ru@PsIL catalyst having ruthenium in the metallic state only confirmed by Ru 3p3/2 at ~462.15 eV and Ru 3p1/2 at ~484.18 eV (Figure 2).



Figure 2 XPS spectrum (Ru 3p1/2 and Ru 3p3/2) of Ru@PsIL catalyst.

The shape and size of the Ru NPs were further characterized by using the transmission electron microscopy (TEM) analyses (Figure 3). The spherical and irregular spherical Ru NPs having the uniform particle size 3 to 6 nm is clearly observed in the TEM images. The majority of Ru NPs ranging 3 to 4 nm while, a small amount of 5 nm Ru NPs also observed on PsIL (ESI, Figure S-3). The thermal stability of any catalyst is important to avoid the product contamination by the degradation of the catalyst. Thus, we investigated the catalytic stability by using the thermogravimetric analysis (TGA). We have observed that the as-synthesized Ru@PsIL catalyst having high thermal stability up to the 350 °C (ESI, Figure S-1).



Figure 3 (a) and (b) TEM images of the ${\tt Ru}@{\tt PslL}$ showing the very small Ru NPs stabilized onto the support of PslL.

In recent years, there has been increasing interest towards the dehydrogenation of ammonia borane (AB) and its derivatives, which are considered as a potential candidate due to high H₂ storage capacity, nontoxicity and high thermal stability.^[44-45] Recently, various nanoparticles have been synthesized and applied as catalysts for the dehydrogenation of AB.^[46,47] Although there are very few reports available on the utilization of AB for transfer hydrogenation reaction of organic compounds,^[48-53] hence,

FULL PAPER

there is a need to explore the more active catalytic systems for the tandem dehydrogenation and transfer hydrogenation reactions. The N-formamides are the very important class of organic compounds, ^[32] which are extensively used in the field of organic synthesis. Due to their intriguing application as various biological intermediates and raw materials for the synthesis of various chemicals,^[33] several catalytic methods have been developed for the synthesis of N-formamides.^[34] Among all the reported methods, the synthesis of Nformamides by using the CO₂ reduction method is considered as one of the most prominent pathways from the industry as well as academic point of view, where various reducing agents such as $H_{2,1}^{[35-36]}$ silane,^[37-42] and borane are being used repeatedly.^[43]

Initially, the formylation of N-methyl aniline (1a) to N-methyl-N-phenylformamide (2a) was selected as a challenging substrate for the optimization of the reaction parameters (Table 1). The reactions were performed with 5 mg of Ru@PSIL catalyst, 1 mmol of 1a, 2 MPa of CO₂ and 3 mmol of the dimethylamine borane (DMAB) by using the K₂CO₃ as a base, at 100 °C for 12 h. Initially, the reaction was performed under the solvent-free conditions and only 40 % of 2a was observed (Table 1, entry 1). Then, to our delight, the use of THF as a solvent provided the 74 % yield of 2a (Table 1, entry 2). The use of CH₃CN as solvent provided 69 % yield of 2a (Table 1, entry 3). However, the use of polar solvents such as DMF and ethanol provided 78 and 71 % yield of 2a, respectively (Table 1, entries 4-5). While, use of a nonpolar solvent such as Toluene, provided a good yield of 2a (70 %) (Table 1, entry 6). Later, we utilized water as a green solvent, and about 80 % was observed (Table 1, entry 7). Next, by considering the solubility of the reactant and DMAB, we utilized the mixture of water and ethanol in 1:1 ratio and surprisingly excellent yield (about 93 %) of 2a was noted (Table 1, entry 8). After the solvent study, we studied the effect of temperature on reaction system (Table 1, entries 9-11). By decreasing the temperature of the reaction system at 80 °C, still same yield of 2a was noted (Table 1, entry 9). Further decreasing temperature up to 60 °C, decreased the yield (68 %), (Table 1, entry 10). Since, we have observed that only 48 % yield of 2a was observed at the room temperature (Table 1, entry 11), we concluded that the 80 °C of temperature is the optimum temperature for the efficient conversion of 1a. Next, the effect of time on the reaction conditions was studied and it was observed that same yield of 2a was noted when reaction proceeds up to 6 h (Table 1, entry 13 entry). By further decreasing time, the decreased yield of 2a has been observed (Table 1, entry14). Next, the effect of the pressure of CO₂ on the reaction system has been explored (Table 1, entries 15-18). By decreasing the pressure of CO₂ to 1 MPa, the decreased amount of 2a was noted (Table 1, entry 15). No, any further improved yield of 2a could be attained by further increasing the CO₂ pressure

from 1 MPa to the 5 MPa(Table 1, entries 16-18), hence, we concluded that the 2 MPa pressure

Table 1 Optimization of the reaction conditions for the N-formylation reaction.^[a]

	H N 1a	CO2 + DMAE	3 <u>Ru@</u> 7,		N H 2a	,O
Entry	Solvent	Temp. (°C)	Time (h)	CO ₂ (MPa)	Yield (%) ^[b]	TON/TOF (h ⁻¹) ^[h]
1	-	100	10	2	40	-
2	THE	100	10	2	74	246/24.6
3	CH ₃ CN	100	10	2	69	230/23
4	DMF	100	10	2	80	266/26.6
5	EtOH	100	10	2	75	250/25
6	Toluene	100	10	2	70	233/23.3
7	Water	100	10	2	80	266/26.6
8	Water:EtOH	100	10	2	93	310/31
9	Water:EtOH	80	10	2	93	310/31
10	Water:EtOH	60	10	2	68	226/22.6
11	Water:EtOH	R.T.	10	2	48	160/16
12	Water:EtOH	80	8	2	93	310/38.7
13	Water:EtOH	80	6	2	93	310/51.6
14	Water:EtOH	80	3	2	41	136/68.3
15	Water:EtOH	80	6	1	70	233/38.8
16	Water:EtOH	80	6	3	92	306/51.1
17	Water:EtOH	80	6	4	94	313/52.2
18	Water:EtOH	80	6	5	94	313/52.2
19 ^[c]	Water:EtOH	80	6	2	18	-
20 ^[d]	Water:EtOH	80	6	2	71	236/39.4
21 ^[e]	Water:EtOH	80	6	2	69	138/23
22 ^[f]	Water:EtOH	80	6	2	78	780/130
23 ^[g]	Water:EtOH	80	6	2	15	-

^[a] Reaction Conditions: 1a (1 mmol), Ru@PSIL (5 mg), CO₂ (2 MPa), DMAB (3 mmol), Water:EtOH (3:3 ml) and K₂CO₃ (0.5 mmol). ^[b] Isolated yields. ^[c] Without catalyst. ^[d] Triethylamine borane. ^[e] Ru/C (10 mg). ^[f] RuCl₃ (10mg). ^[g] PSIL (10mg). [h] TON per h.

of CO_2 was the optimum temperature to provide the effective product. Next, the reaction was carried out without the catalyst and no significant conversion of **2a** noted (Table 1, entry 19). When we used triethylamine borane as a reducing agent instead

FULL PAPER

Table 2 Substrate study for the formylation reactions.[a]

Entry	Substrate	Product	Yield (%) ^b	TON	TOF ^[e] h ⁻¹
1	HZ	⊢N → H	93	310	51.6
2	0 NH	N H	99	330	55
3	NH	N H	99	330	55
4	NH	N-C	96	320	53.3
5	NH N		96	320	53.3
6	`NH │	N N H	89	296	49
7	NH	NH	84	280	46.6
8	n-Bu NH n-Bu	n-Bu O n-Bu H	80	266	44.4
9 ^c			71	236	39.4
10	N H		82	273	45.5
11	NH ₂	NH O H	75	250	41.6
12 ^c	Ph N Ph H	Ph N Ph	45	150	6.25
13	NH ₂	HNH	72	240	40
14	NH ₂	С ^Н ^н	80	266	44.4
15	N N N N N N N N N N N N N N N N N N N	С – N – H	88	293	48.8
16	H N O		75	250	41.6
17 ^c	Ph NH Ph	Ph O N H	30	100	4.1
18	NH ₂	, N N N N N N N N N N N N N N N N N N N	87	290	48.3
19			84	280	46.6
20 ^d			54	180	30
21 ^d		ССС N H	48	160	26.6
22	П	N H	77	256	42.7

^[a]Reaction conditions: Amine (1 mmol), Ru@PSIL (5 mg), CO₂ (2 MPa), DMAB (3 mmol), Water:EtOH (3:3 ml) and K₂CO₃ (0.5 mmol), temperature (80 °C), Time (6 h). ^[b]isolated yields. ^[a]Time (24 h). ^[d]DMAB (5 mmol). [e] TON per h.

WILEY-VCH

of DMAB the observed yield of **2a** was 71 % (Table 1, entry 20). We also tested the other commercially available heterogeneous catalysts like Ru/C for the formylation reactions, and we have observed the lower yield as compared to the Ru@PsIL (Table 1, entry 21). Next, the use of RuCl₃ as a homogeneous catalytic system showed the 78 % yield which is very low as compared to Ru@PsIL (Table 1, entry 22). In a control experiment, when only polymer support i.e. PsIL was utilized to investigate the catalytic activity and we have observed very low yield of **2a** suggesting the minimum contribution of support in the catalytic activities. The turnover number (TON) and turnover frequency (TOF) of the developed catalyst has been calculated based on the reported method for the soluble metal nanoparticles.^[70]

After the optimization reaction conditions in hands, we have extended this protocol for the formylation of a variety of substrates of amines (Table 2). The N-methyl aniline provides the excellent vield of the formylated product (Table 2, entry 1). The secondary cyclic amines, which are more nucleophile in nature, such as morpholine, piperidine, cyclopentyl amine and 1-methylpiperazine are found to be highly reactive and providing a very excellent yield of the respective formylated products (Table 2, entries 2-5). Then, we tested this methodology for the synthesis the dimethylformamide, a well-known solvent for the organic reactions and interestingly, it was found that dimethyl amine provides the excellent yield (Table 2, entry 6). Other symmetric diamines, such as diethylamine and dibutyl amine was also providing the excellent yield of the corresponding formamides (Table 2, entries 7-8). Then, the symmetric di-cyclic amine such as dicyclohexyl amine showed the slightly decreased yield of Nformylated product which could be possible due to the steric hindrance of cyclohexyl ring (Table 2, entry 9). Methyl-substituted benzylamine and benzylamine also well tolerated under the optimized reaction condition and provide a better yield of formylated products (Table 2, entries 10-11). The symmetric benzylamine like dibenzyl amine gives the moderate yield for the N-formylated product (Table 2, entry 12). The primary cyclic amine like cyclohexylamine was also tested at the optimized reaction condition and good yield of formylated product was noted (Table 2, entry 13). Next, the challenging substrate like aniline for the N-formylation was tested and good yield was noted (Table 2, entry 14). Further, the substituted aniline was formylated and good yield as compared to aniline was noted (Table 2, entries 15-16). While, the use of diphenylamine was found sluggish to formylate and provide very low yield (Table 2, entry 17). The substituted amines at the para-position with electron donating functional group such as p-methoxyaniline provide the good yield of the N-formylated product (Table 2, entry 18). The heterocyclic compound like indoline also tested for the formylation reaction and showed the good yield (Table 2, entry 19). Interestingly, the indole which containing reducible double bond, as well as amine for CO2 for N-formylation, was tested and interestingly, the reduction of the double bond as well as the N-formylated product obtained (Table 2, entry 20). By such encouraging results from the hydrogenation of double bond as well as formylation reactions, we further utilized the isoquinoline ring system to synthesize the biologically important N-formyl-1,2,3,4-tetrahydroisoquinoline, and we observed the moderate yield (Table 2, entry 21). Also, the

FULL PAPER

direct use of 1,2,3,4-tetrahydroisoquinoline provided the excellent yield of *N*-formyl-1,2,3,4-tetrahydroisoquinoline (Table 2, entry 22).

After the successful synthesis of various formylation products, we further extended this catalytic protocol for the cyclization reactions to synthesize heterocyclic compounds. The high activity of Ru@PsIL for N-formylation reaction encouraged us to use this catalyst for the synthesis of bezimidazoles from *o*-phenyl diamine,

 $\ensuremath{\text{Table 3}}\xspace$ Ru@PsIL catalyzed synthesis of benzimidazoles bu using DMAB and CO2.a



^a Reaction conditions: Amine (1 mmol), Ru@PSIL (5 mg), CO₂ (2 MPa), DMAB (3 mmol), Water:EtOH (3:3 ml) and K₂CO₃ (0.5 mmol), Time (18 h). ^b isolated yield. ^C DMAB (5 mmol). N. D (Not detected). CO₂ and DMAB as a reducing agent (Table 3). The benzimidazoles are fundamental intermediates in the synthesis of pharmaceutical scaffolds, and heterocycles with a benzimidazole structure are pervasive in biologically active compounds.^[58-60] Nowadays, much progress has been achieved for the synthesis of benzimidazoles and its derivatives. Still, there is need to develop the efficient catalytic method which works under simple green conditions and utilizes the renewable material rather than the use of toxic harmful chemicals. The direct use of CO2 and ophenylenediamine to synthesize the benzimidazoles are also one of the interesting reactions, as it which utilizes the CO₂ as a C1 source.^[61] Initially, the reaction of an o-phenyl diamine with CO2 (2 MPa) and DMAB (2 mmol) in the presence of Ru@PsIL and water: ethanol (1:10) as the solvent system was utilized, to our surprise we have observed the excellent yield of benzimidazole (Table 3, entry 1). Interestingly, Ru@PsIL catalyzed the reaction of 2nitroaniline with CO₂ in presence of DMAB (5 mmol), have provided the excellent yield of the benzimidazole by reduction of the nitro functional group as well as CO₂ (Table 3, entry 2). The methyl-substituted 1,2-diamine as well as methyl substituted 2-nitroaniline also well tolerated and provide the excellent yield of the methyl substituted benzimidazoles (Table 3, entries 3-4). The 4,6-dimethyl ophenylenediamine also provide the good yield of corresponding benzimidazole (Table 3, entry 5). The Nmethyl substituted diamine and nitroaniline provide the excellent yield of N-methyl benzimidazole (Table 3, entries 6-7). The electron donating group such as 4-methoxy ophenyldiamine and 4-methoxy 2-nitroaniline also provided the good yield (Table 3, entries 8-9). While, the electron withdrawing group such as chloro on 2-nitroaniline was found sluggish to react (Table 3, entry 10). While, the methyl at the ortho position of diamine also provide the good yield (Table 3, entry 11). The use of 2-aminophenol as starting material



Figure 4 Recyclability of Ru@PsIL catalysts for the N-formylation 1a to the 2a at the optimized reaction conditions.

FULL PAPER

provided only 15% yield of benzoxazolidinone suggesting the role of electron withdrawing groups on catalytic activity (Table 3, entry 12). No, any bezoxazolidinones was noted when 2-nitrophenol was utilized as a substrate (Table 3, entry 13). The recyclability of any heterogeneous catalysts plays the crucial role to determine the suitability of the developed catalysts for the industrial applications.^[62] The recyclability of developed catalysts was investigated for the formylation reaction of 1a to 2a at the optimized reaction conditions (Figure 4). The developed catalyst shows excellent recyclability up to five recycle run with a negligible loss in yield suggesting the promise of this reported methodology towards the efficient and recyclable catalyst for the industrial applications. The leaching of catalyst was also investigated and very low leaching of Ru metal noted (0.1%). Finally, after the fifth recycle study we characterized the Ru@PsIL catalyst by using SEM analyses (ESI, Figure S-2). After the eight recycle runs the stability of Ru@PsIL catalysts investigated by using TGA analysis. The slightly decreased stability of catalyst as compared to as-synthesized catalysts noted (ESI, figure S1). While, very negligible shrinkage on the polymer support observed, which indicates the high stability and good recyclability of the catalyst.

Comparison our method with other approaches

The comparisons of our reported method with recently reported methods used for the utilization of CO₂ as a C1 source for the formylation and cyclization reaction are summarized in Table 1 (ESI, S1). Although, the use of H_2 as a clean energy source is reported for the reduction reactions the utility of H₂ for reactions may be problematic due to their explosive nature, the demand of elevated temperature and high pressure and requirement of expensive transition metal complexes for the reduction reactions.[36],[63] Although, the silanes are well reported and active reducing agent for these type of reactions, they are low atom-economical and require an expensive catalyst.^{[36],[65]} In case of silane, most of the reaction systems are non-recyclable and expensive as compared to the borane.[66]-[68] In case of heterogeneous catalysts, the use of silane as reducing agents is problematic due to the generation of solid waste, which is not soluble in water and in common solvents. The use of toxic solvents in these processes makes complications in catalyst separation. In these circumstances, the use of borane is considered as an ideal compared to gaseous hydrogen and silanes due to the high hydrogen storage capacity, good air and moisture stability and easy to handling.

Conclusions

In conclusion, we have synthesized highly efficient, novel Ru@PsIL as a heterogeneous catalytic protocol which utilizes CO_2 for the N-formylation of amines and synthesis of

benzimidazoles using DMAB as a green and mild reducing agent. This synthesized catalyst shows diverse active centers such as stable organic support and ionic environment which is helpful for the stabilization of small nanoparticles, which regulates the diffusion of the substrate and product from active centers very easily. The developed methodology is highly efficient and sustainable due to the use of DMAB as a safe and atom economic hydrogen source, mild CO₂ pressure, low temperature and utilization of water: ethanol as a green solvent system. Interestingly, Ru@PsIL catalyst able to the tandem reduction of the double bond of indole and isoquinoline to indoline-1-carbaldehyde and biologically important N-formyl-1,2,3,4tetrahydroisoquinoline respectively. Additionally, this developed methodology facilitates to provide a large number of N-formylated and cyclized product of benzimidazoles with tandem nitro reduction, with excellent recyclability.

Experimental Section

Synthetic method for the preparation of PsIL

The synthesis of Ru@PsIL catalyst has been performed by modifying the reported procedure (ESI, S-2).^[28-30] Typically, the Ru@PsIL has been synthesized by the immobilization of Merrifield peptide resin with 1,2-dimethyl-1*H*-imidazole to give PsIL (Scheme 2). For this the simple and efficient method utilized for the immobilization of ILs in which Merrifield peptide resin (2% cross-linked, 2.3 mmol Cl/g, Aldrich) (1 g, 5.34 mmol), was suspended 1,2-dimethyl-1*H*imidazole (10 mL) in Toluene (25 mL) as solvent at 100 °C for 10 h. Then the PsIL was filtered, washed with DMF (3 x 20 mL), MeOH (3 x 20 mL), CH₂Cl₂ (3 x 20 mL) and dried under vacuum at 60 °C for 12 h.

General procedure for the immobilization of Ru@NPs onto PsIL

The as-synthesized PsIL (100 mg,) was suspended in a round-bottomed flask containing 2 mL of deionized water, 2 mL of ethylene glycol and RuCl₃ (20.7 mg), and stirred at room temperature for 6 h. Then the NaBH₄ (1 mmol) was dissolved water (20 ml) and slowly added with continuous stirring at the 5 °C. The suspension then stirred for 4 h. for the complete reduction and resulted in material filtered and washed with deionized water (3 x 2.0 mL) and MeOH (1 x 1.70 mL). Finally, the polymer was vacuum dried at 80 °C till constant weight. The percentage of loading of ruthenium NPs on polymer support calculated by using the ICP-AES analysis and 6.076 % of Ruthenium metal observed on the polymer.

Experimental procedure for the formylation and cyclization reactions

The N-formylation and cyclized product were synthesized by the reaction amines with CO_2 and dimethylamine borane (DMAB) in the presence of the Ru@PsIL catalyst. All the

Manuscr

FULL PAPER

reactions were carried out in a 100 mL stainless-steel autoclave with stirring at 600 rpm and equipped with an automatic stirrer and temperature control system. In a typical reaction procedure, the catalyst (5 mg) was introduced into the reactor containing amine (1 mmol), Water: EtOH (3:3 ml) and DMAB (2 mmol) at room temperature and then pressurized to the respective pressure of CO₂ and heated to a particular temperature. After completion of the reaction, the reactor was cooled in an ice-cold water bath and then CO2 was released slowly. The synthesized products were extracted and purified by using silica column chromatography using the pet ether and ethyl acetate and H¹ & C¹³ spectra were recorded.

Acknowledgments

The author Vitthal Saptal acknowledges to the University Grant Commission (UGC), for providing the Senior Research Fellowship (SRF).

Keywords: Carbon dioxide • Ionic Liquids • Reduction • Nanoparticles• Green solvents

- [1] https://www.co2.earth/global-co2-emissions;
- [2] Carbon Dioxide as Chemical Feedstock, ed. M. Aresta, Wiley-VCH, 2010
 [3] B. M. Bhanage, M. Arai (Eds.), Transformation and Utilization of Carbon
- Dioxide, Springer-Verlag, Berlin, Heidelberg, 2014, p. 4-29;
- [4] (a) A. Kleij, M. North; and A. Urakawa, *ChemSusChem*, **2017**, 10, 1036-1038; (b) M. Liu, L. Liang, X. Li, X. Gao and J. Sun, *Green Chem.*, **2016**,18, 2851-2863; (c) M. Liu, X. Lu, L. Shi, F. Wang, and J. Sun, *ChemSusChem* **2016**, 9, 1-11; (d) M. Liu, J. Lan, L. Liang, J. Sun M. Arai, J. of Catal., **2017**, 347, 138-147; (e) M. Liu, K. Gao, L. Liang, J. Sun, L. Sheng and M. Arai, *Catal. Sci. Technol.*, **2016**, 6, 6406-6416.
- [5] J. W. Comerford, I. D. V. Ingram, M. North, X. Wu, Green Chem. 2015, 17, 1966–1987.
- [6] Q. Liu, L. Wu, R. Jackstell and M. Beller, Nat. Commun., 2015, 6, 5933-5947.
- [7] P. Xu, X. Han, B. Zhang, Y. Du, H.-L. Wang, Chem. Soc. Rev. 2014, 43, 1349–1360.
- [8] P. Zhao, N. Li, D. Astruc, Coord. Chem. Rev. 2013, 257, 638-665.
- [9] L. L. Chng, N. Erathodiyil, J. Y. Ying, Acc. Chem. Res. 2013, 46, 1825-1837.
- [10] V. Montes-García, J. Pérez-Juste, I. Pastoriza-Santos, L. M Liz-Marzán, Chem. - Eur. J. 2014, 20, 10874-10883.
- [11] R. White, R. Luque, V. Budarin, J. Clark and D. Macquarrie, *Chem. Soc. Rev.*, 2009, 38, 481.
- [12] P. Wasserscheid and T. Welton, in Ionic Liquids in Synthesis, Wiley-VCH, Weinheim, 2007
- [13] C. Mehnert, Chem.-Eur. J., 2005, 11, 50-56.
- [14] A. Riisager, F. Haumann and P. Wasserscheid Eur. J. Inorg. Chem., 2006, 695-706
- [15] Y. Gua and G. Li, Adv. Synth. Catal., 2009, 351, 817-847.
- [16] J. Dupont and J. Scholten, Chem. Soc. Rev., 2010, 39, 1780-1804.
- [17] K. Luska, P. Migowski, S. Sayed and W. Leitner, *Angew. Chem. Int. Ed.* 2015, 54, 15750-15755.
- [18] F. Giacalone and M. Gruttadauria, ChemCatChem, 2016, 8, 664-684.
- [19] K. Luska P. Migowskia and W. Leitner, Green Chem., 2015, 17, 3195.

- [20] K. Luska, P. Migowski, S. Sayed and W. Leitner, ACS Sustainable Chem. Eng., 2016, 4, 6186.
- [21] M. Prog, Polym. Sci. 2011, 36, 1629-1648.
- [22] J. Yuan, M. Antonietti, Polymer, 2011, 52, 1469-1482.
- [23] M. Pereira, *Curr. Org. Chem.*, **2012**, 16, 1680-1710.
- [24] J. Yuan, S. Wunder, F. Warmuth, Y. Lu, Polymer, 2012, 53, 43-49.
- [25] X. Yang, Z. Fei, D. Zhao, W. H. Ang, Y. Li, P. J. Dyson, *Inorg. Chem.* 2008, 47, 3292-3297.
- [26] R. L. Weber, Y. S. Ye, A. L. Schmitt, S. M. Banik, Y. A. Elabd, *Macromolecules*, 2011, 44, 5727–5735
- [27] P. Zhang, T. Wu, B. Han, Adv. Mater. 2014, 26, 6810-6827.
- [28] M. I. Burguete, E. Garcia-Verdugo, S. V. Luis, J. A. Restrepo, *Phys. Chem. Chem. Phys.* 2011, 13, 14831-14838.
- [29] S. Montolio, C. Vicent, V. Aseyev, I. Alfonso; H. Burguete Tenhu, E. García-Verdugo and S. Luis, ACS Catal., 2016, 6, 7230–7237.
- [30] (a) J. Restrepo, R. Porcar, P. Lozano I. M. Burguete, E. Verdugo and S. Luis, *ACS Catal.* 2015, 5, 4743-4750; (b) E. Verdugo, B. Altava, M. I. Burguete; P. Lozano and S. Luis, *Green Chem.*, 2015, 17, 2693-2713
- [31] (a) T. Gutel, C. C. Santini, K. Philippot, A. Padua, K. Pelzer, B. Chaudret, Y. Chauvin and Jean-Marie Basset, *J. Mater. Chem.*, **2009**, 19, 3624-3631; (b) M. H. G. Prechtl, M. Scariot, J. D. Scholten, G. Machado, S. R. Teixeira, and J. Dupont, *Inorg. Chem.*, **2008**, 47, 8995-9001; (c) P. S. Campbell, C. C. Santini, F. Bayard, Y. Chauvin, V. Collière, A. Podgoršek, M. F. Costa Gomes, J. Sá, *J. Catal.* **2010**, 275, 99-107.
- [32] A. Jackson and O. Meth-Cohn, J. Chem. Soc., Chem. Commun., 1995, 1319-1319.
- [33] V. Das, R. Devi, P. Raul and A. Thakur, *Green Chem.*, **2012**, 14, 847–854
- [34] T. M. E. Dine, D. Evans, J. Rouden, J. Blanchet, Chem. Eur. J. 2016, 22, 5894-5898.
- [35] X. Cui, Y. Zhang, Y. Deng, and F. Shi, Chem. Commun., 2014, 50, 189-191.
- [36] L. Zhang, Z. Han, X. Zhao, Z. Wang and K. Ding, *Angew. Chem., Int. Ed.*, 2015, 54, 6186-6189.
- [37] O. Jacquet, C. Das Neves Gomes, M. Ephritikhine, & T. Cantat, J. Am. Chem. Soc. 2012, 134, 2934-2937.
- [38] O. Jacquet, X. Frogneux, C. Das Neves Gomes & T. Cantat, Chem. Sci. 2013, 4, 2127-2131.
- [39] C. Chong and R. Kinjo, Angew. Chem. Int. Ed. 2015, 54, 12116-12120.
- [40] X, Liu, R. Ma, C, Qiao, H, Cao and L. He, Chem. Eur. J., 2016, 22, 1-6.
- [41] C, Chauvier, T. Cantat, ACS Catal. 2017, 7, 2107-2115.
- [42] X. Liu, X. Li, C. Qiao H. Fu and L. He, Angew. Chem., 2017, 129, 7533-7537.
- [43] V. Saptal, B. Bhanage, ChemSusChem, 2016, 9, 1980-1985.
- [44] T. He, P. Pachfule, H. Wu, Q. Xu and P. Chen, Nat. rev. 2016, Doi:10.1038/natrevmats.2016.59.
- [45] P. Pachfule, X, Yang, Q. Zhu, N. Tsumori, T, Uchida and Q. Xu, J. Mater. Chem. A, 2017, 5, 4835-4841.
- [46] W. Zhan, Q. Zhu; and Q. Xu, ACS Catal. 2016, 6, 6892-6905.
- [47] M, Bluhm, M. Bradley, R. Butterick, U. Kusari and L. Sneddon J. Am. Chem. Soc., 2006, 128, 7748-7749.
- [48] a) E. Korytiakova, N. Thiel, F. Pape and J. Teichert, *Chem. Comm.* 2017, 53, 732-735; b) T. Zhao, G. Zhai, J. Liang, P. Li, X. Hu and Y. Wu, *Chem. Commun.*, 2017, 53, 8046-8049.
- [49] Y. Jiang and H. Berke, Chem.Comm., 2007, 3571-3573.
- [50] N. Patil T. Sasaki, and B. M. Bhanage, RSC Adv., 2016, 6, 52347-52352.
- [51] P. Justin, J. Stelmach and R. Waterman, Dalton Trans., 2015, 44, 12074.
- [52] N. Patil, M. Bhosale, B. M. Bhanage, *RSC Adv.*, **2015**, 5, 86529-86535.
- [53] D. B. Nale, D. Rath, K. M. Parida, A. Gajengi and B. M. Bhanage, *Catal. Sci. Technol.*, **2016**, 6, 4872-4881.
- [54] V. B. Saptal, D. B. Shinde, R. Banerjee, B. M. Bhanage, *Catal. Sci. Technol.*, **2016**, 6, 6152-6158.
- [55] V. B. Saptal, T. Sasaki, K. Harada, D. Nishio-Hamane and B. M. Bhanage, *ChemSusChem*, **2016**, 9, 644–650. s
- [56] V. B. Saptal, B. M. Bhanage, ChemCatChem., 2016, 8, 244-250.

FULL PAPER

- [57] V. B. Saptal and B. M. Bhanage, ChemSusChem, 2016, 10, 1145–1151.
- [58] C. G. Mortimer, G. Wells, J. P. Crochard, E. L. Stone, T. D. Bradshaw, M. F. G. Stevens and A. D. Westwell, *J. Med. Chem.*, **2006**, 49, 179-185
- [59] C. S. Lin, R. Q. Zhang, C. S. Lee, T. A. Niehaus and T. Frauenheim, J. Phys. Chem. B, 2006, 110, 20847- 20851.
- [60] J. Bhaumik, Z. Yao, K. E. Borbas, M. Taniguchi and J. Lindsey S. Masked, J. Org. Chem., 2006, 71, 880.
- [61] A. Tlili, E. Blondiaux, X. Frogneux and T. Cantat, *Green Chem.*, 2015, 17, 157.
- [62] A. Thomas, Angew. Chem. Int. Ed. 2010, 49, 8328.
- [63] P. Daw, S. Chakraborty, G. Leitus, Y. Diskin-Posner, Y. Ben David, D. Milstein, ACS Catal. 2017, 7, 2500-2504.
- [64] P. Ju, J. Chen, A. Chen, L. Chen and Y. Yu, ACS Sustainable Chem. Eng., 2017, 5, 2516-2528.
- [65] T. V. Q. Nguyen, W. Yoo and S. Kobayashi, Angew. Chem. Int. Ed. 2015, 54, 9209-9212.
- [66] L. Hao, Y. Zhao, B. Yu, Z. Yang, H. Zhang, B. Han, X. Gao and Z. Liu, ACS Catal. 2015, 5, 4989-4993.
- [67] B. Yu, H. Zhang, Y. Zhao, S. Chen, J. Xu, C. Huang and Z. Liu, Green Chem., 2013, 15, 95-99.
- [68] O. Jacquet, C. D. N. Gomes, M. Ephritikhine and T. Cantat ChemCatChem., 2013, 5, 117–120.
- [69] C. Antonetti, M. Oubenali, A. M. R. Galletti, P. Serp, G. Vannucci, Applied Catalysis A:General, 2012, 421, 99-107
- [70] A. P. Umpierre, E. d. Jesffls, and J. Dupont, *ChemCatChem.*, 2011, 3, 1413-1418

FULL PAPER

FULL PAPER



The highly active Ru NPs supported on polymeric ionic liquids and utilized for Nformylation and cyclization reactions at mild reaction conditions. Vitthal B. Saptal, Takehiko Sasaki and Bhalchandra M. Bhanage*

Page No. – Page No. Ru@PsIL Catalysed synthesis of Nformamides and benzimidazole using Carbon Dioxide and Dimethylamine Borane