

PROJECT COMPLETION REPORT

- Notes:
1. 3 copies of the Project Completion Report (PCR) should be sent within one month of the completion or termination of the project.
 2. The PCR should be in bound form.
 3. Cover page should include the title of the project, file number, names and addresses of the investigation.

1. Title of the project: *Green and sustainable catalysts based on zeolite for oxidative transformation reactions*
2. Principal Investigator(s) and Co-Investigator(s): Dr. Utpal Bora (PI) and Dr. Pankaj Bharali (CoPI)
3. Implementing Institution(s) and other collaborating Institution(s): Tezpur University, Department of Chemical Sciences, Tezpur University, Napaam, Tezpur, Assam, India 784028
4. Date of commencement: 18/09/2019
5. Planned date of completion: 17/09/2021
6. Actual date of completion: 17/09/22
7. Objectives as stated in the project proposal:
The proposed project will be undertaken with the following objectives:
 - i) Synthesis of zeolite from renewable sources such as rice husk ash and coal fly ash to obtain a renewable multipurpose heterogeneous catalyst that is active, versatile and stable under the process conditions and which can compete with currently employed commercial catalysts for the VOC oxidation reactions.
 - ii) Modification of the renewable zeolite surface and immobilization of metal and metal nanoparticles (Pd and Cu) to make renewable zeolite as a heterogeneous catalyst for C-C, C-O and C-N bond formation reactions.
 - iii) Preparation of Pd/Cu bimetallic zeolite based heterogeneous catalyst for C-C, C-N and C-O bond formation and VOC oxidation reactions.
 - iv) Understanding the structure-property relation and mechanistic studies for the above mentioned catalytic processes.
8. Deviation made from original objectives if any, while implementing the project and reasons thereof: No
9. Experimental work giving full details of experimental set up, methods adopted, data collected supported by necessary table, charts, diagrams & photographs:

To achieve the proposed objectives, following reactions were carried out:

General procedure for preparation of Cu₂O/Cu nano-particles (NPs): Papaya peel (10 g) was washed with distilled water, finely chopped and then wet ground with 100 mL distilled water. The extract was filtered through a sintered glass crucible. In a 100 mL Teflon-lined stainless steel autoclave, 0.5 g Cu(OAc)₂ was mixed with 40 mL papaya peel extract. The mixture was allowed to stir for 30 min to obtain a homogeneous solution of Cu(OAc)₂. Thereafter, the resulting mixture was sealed and subjected to heating at 160°C for 7h.

In a similar manner, another reaction mixture was prepared and allowed to heating at 190°C for 7 h. It is observed that the hydrothermal heating of Cu(OAc)₂/papaya peel extract mixture at 160 °C (Cu-433K) produced reddish brown precipitate whereas brownish black precipitate was obtained at 190°C (Cu-463K). Both resulting residues (NPs) were separated by centrifugation, washed several times with distilled water and ethanol and dried in vacuum for further analytical experiments (Figure 1).

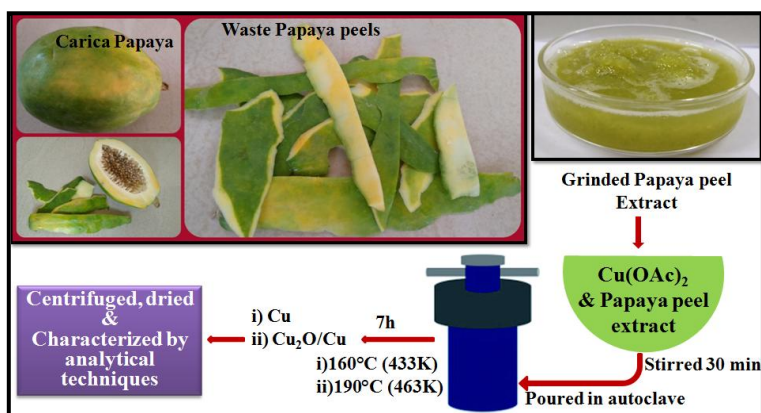


Figure 1. Preparation of Cu NPs using papaya peel extract.

Characterizations of the synthesised Cu NPs

Initially, we have performed solid state UV/Vis spectroscopic experiment and evident the appearance of the broad band due to surface plasmon resonance of the Cu NPs at 500 nm which reveals the formation of Cu NPs (Figure 2, left). Further, we have performed powder X-ray diffraction (p-XRD) analyses for both the Cu NPs (Cu-433K and Cu-463K) (Figure 2, right) to understand the crystalline nature of the NPs. The powder XRD pattern for Cu-433K is identical to that of pure Cu (JCPDS- 85-1326) which resembles a fcc structure. The diffraction pattern is observed at 2θ values 43.2°, 50.3° and 74.1° corresponding to crystal planes (111) (200) and (220). The sharp peaks indicate its highly crystalline nature. A slight difference in p-XRD pattern of Cu-463K was observed with an additional weak peak at a 2θ value of 36.4° with the reflection of (111) plane of cubic Cu₂O nanostructure (JCPDS-78-2076). The diffraction peaks ascribed to Cu₂O is due to the *in situ* transformation of Cu to Cu₂O on increasing the temperature. This is because, pure Cu does not react with water but, instead it reacts with steam to give hydrogen gas and metal oxides. So, on being subjected to high temperature, the oxidation of Cu occurs with increasing water vapour pressure due to the increased Cu vacancy. As such at 190

°C, most of the water molecules are in their vapour state leading to oxidation of some Cu(0) species to Cu₂O.¹

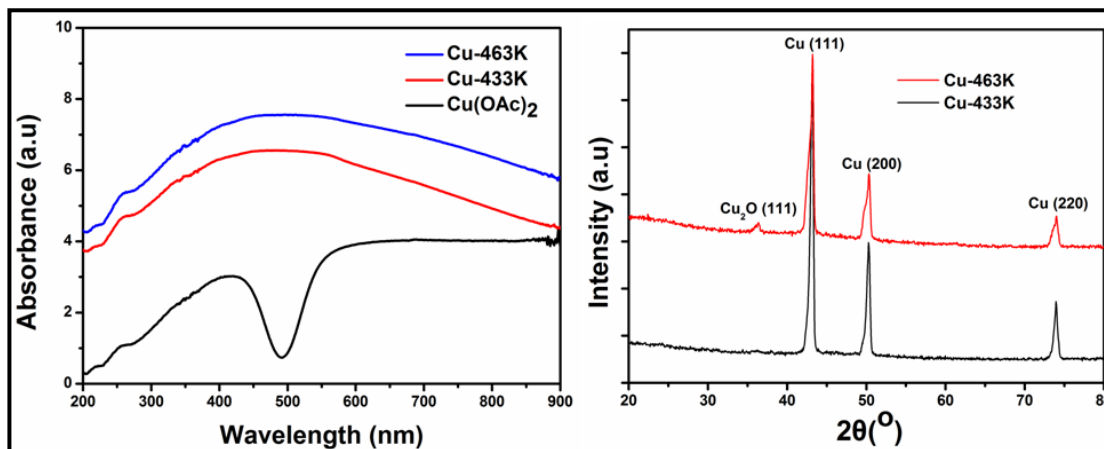


Figure 2. (left) Solid state UV/Vis spectra of, Cu-433K and Cu-463K; (right) Powder XRD pattern of Cu(OAc)₂, Cu-433K and Cu-463K.

FTIR spectrum of the Cu(OAc)₂ and Cu-463K were recorded (Figure 3a and 3b). The diminished vibrational modes due to absence of metal-ligand interaction in the region of 1000-500 cm⁻¹ for Cu-463K signifies the decomposition of Cu(II) species. Energy dispersive X-ray (EDX) analysis of the Cu-463K reveals the presence of Cu and O, which is devoid of any other impurities (Figure 3, right).

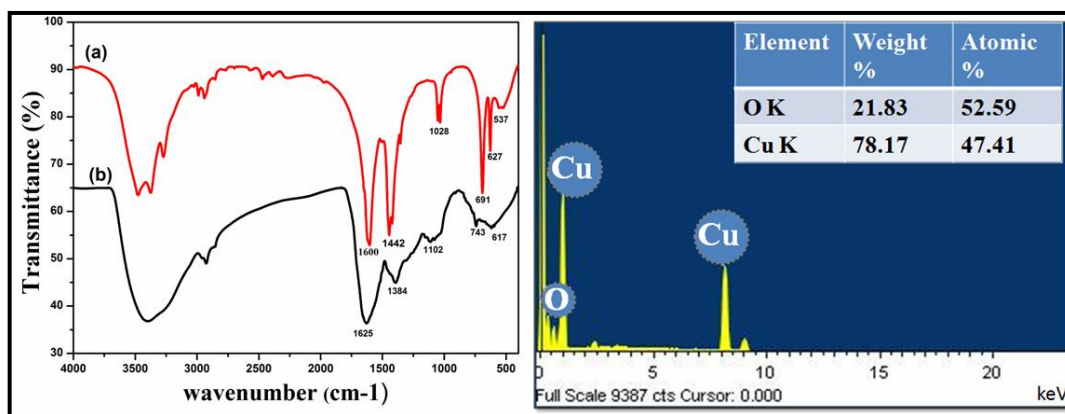


Figure 3. (left) FTIR spectra of (a) Cu(OAc)₂ and (b) Cu-463K NP; (right) EDX analysis of Cu-463K NPs.

Further, the Cu-463K was assessed *via* energy dispersive spectroscopy (EDS) mapping which confirms the corresponding elemental distribution of the sample. The respective elemental mapping for Cu and O are presented in Figure 4.

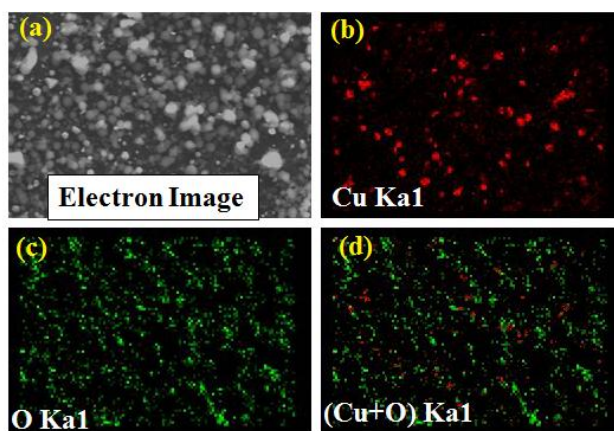


Figure 4. EDS maps (a) electron image (b) Cu distribution (c) O distribution (d) Cu and O distribution of Cu-463K

The surface characteristic of the Cu-463K NPs was identified by scanning electron microscopy (SEM) images (shown in Figure 5a, b and c). It can be seen that the smaller particles of Cu_2O are stacked above the spherical $\text{Cu}(0)$ NPs. It is also seen from Fig. 5b, c that $\text{Cu}_2\text{O}/\text{Cu}$ NPs surface are porous in nature.

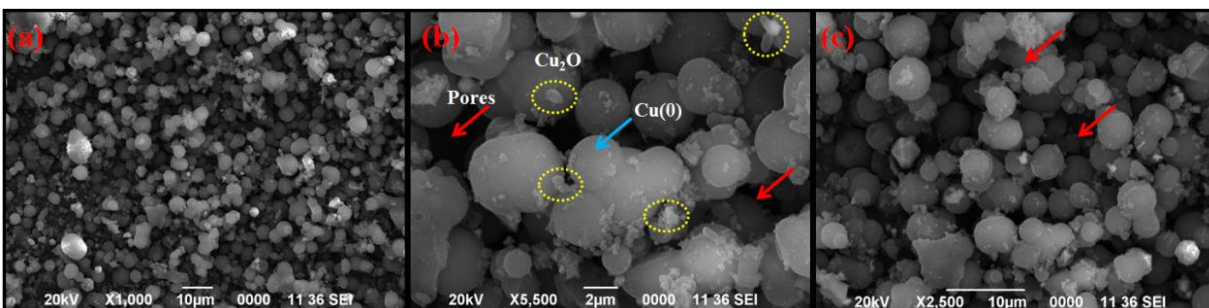


Figure 5. (a, b and c) are the SEM images of Cu-463K.

The bulk morphology was investigated by TEM analysis. Two different Cu phases can be distinguished which represent $\text{Cu}(0)$ and Cu_2O particles (Figure 6a, b and c). Both the copper phases and particles are distributed like lamellar sheets stacked one above the other. From the HRTEM images, the two phases could be distinguished which showed lattice fringes with an interlayer spacing of 0.20 nm and 0.25 nm due to the (111) lattice plane of Cu and Cu_2O , respectively (Figure 6d). Moreover, the inset in Figure 6c, represents the SAED pattern with four well resolved rings corresponding to (111), (220), (200) and (311) reflection of face centered cubic (fcc) lattice of Cu NPs.

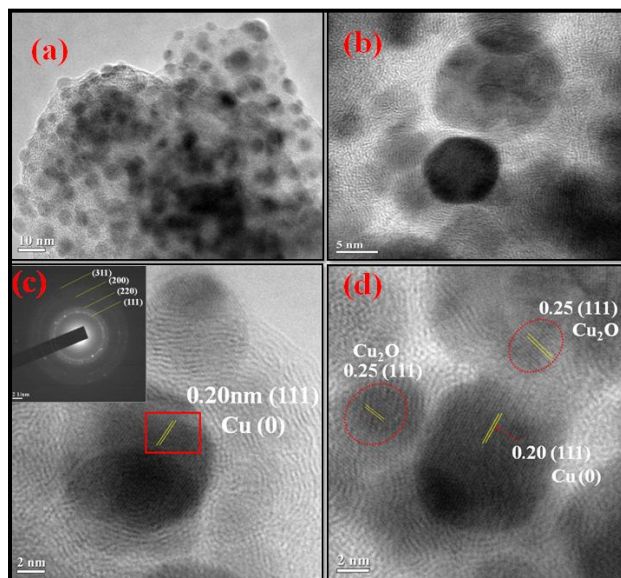


Figure 6. (a, b, c and d) are the TEM and HRTEM images and inset in(c) SAED pattern of the Cu-463K NPs

In order to examine the porous behaviour and to evaluate the surface area and pore size distribution of Cu-463K, BET surface analysis technique was employed (Figure 7). From the nitrogen adsorption-desorption (BET) experiment, it was found that the curve belonged to the type IV isotherm with distinct H3 hysteresis loops. Hysteresis above $P/P_0 \sim 0.6$ (N_2 @ 77K) is due to the presence of the mesopores. Further, the surface area of the Cu-463K NPs as calculated by the BET equation was about $45.249 \text{ m}^2/\text{g}$ with pore volume $0.176 \text{ cm}^3/\text{g}$ and an average BJH pore diameter of 9.864 nm . Moreover, the pore size distribution curve (inset) also indicates the mesoporosity of the $\text{Cu}_2\text{O}/\text{Cu}$ NPs (Cu-463K).

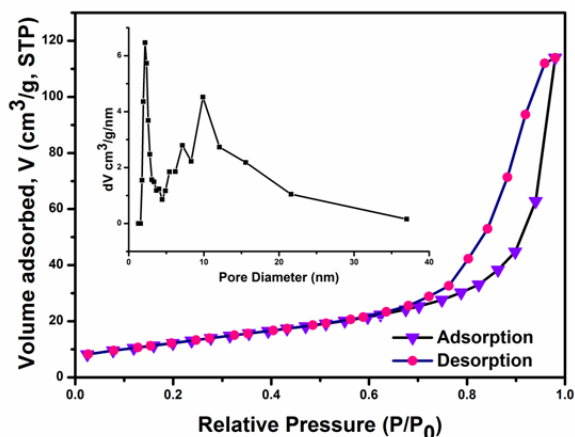
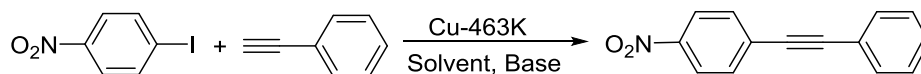


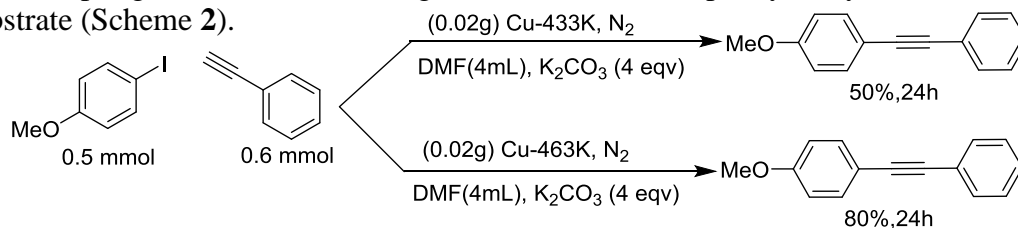
Figure 7. BET surface area and pore size distribution (inset) of Cu-463K.

The catalytic activity of the newly developed Cu NPs will be explored in the Sonogashira cross-coupling reaction (Scheme 1).



Scheme 1. Representative scheme for Sonogashira cross-coupling reaction

Initially, the catalytic activities of the copper NPs were investigated for Sonogashira cross-coupling reaction considering 4-Iodoanisole and phenylacetylene as the model substrate (Scheme 2).



Scheme 2. Controlled experiment for Sonogashira cross-coupling

From the controlled experiment for Sonogashira cross-coupling, it was found that Cu-463K provides greater catalytic activity. This is due to the *in situ* formation of Cu₂O, which results in a synergistic interaction between Cu(0) and Cu(I) ion, leading to greater catalytic activity in the coupling reaction.¹ The efficiency of Cu₂O/Cu NPs (Cu-463K) was examined in Sonogashira coupling reaction considering different reaction parameters. The cross coupling between 4-Iodonitrobenzene and phenylacetylene was taken as the model reaction and using Cu-463K (20 wt%) as the catalyst, the reaction was studied by varying the solvent system, catalyst loading, bases and temperature (Table 1).

Table 1. Optimization of catalytic system for Sonogashira cross-coupling reaction ^[a]

Entry	Cu-463K (wt%)	Base (mmol)	Solvent (mL)	Temp. (°C)	Time (h)	Yield (%) ^[b]
Solvents effect						
1	20	K ₂ CO ₃	Water	90	24	20
2	20	K ₂ CO ₃	EtOH	80	24	50
3	20	K ₂ CO ₃	1,4-Dioxane	90	24	nr
4	20	K ₂ CO ₃	EtOH/H ₂ O(1:1)	90	24	40
5	20	K ₂ CO ₃	DMF	90	12	92
Catalyst loading						
6	5	K ₂ CO ₃	DMF	90	24	40
7	10	K ₂ CO ₃	DMF	90	12	90
8	15	K ₂ CO ₃	DMF	90	12	90
Different bases						
9	10	Cs ₂ CO ₃	DMF	90	12	88
10	10	Na ₂ CO ₃	DMF	90	24	Trace
11	10	NaOH	DMF	90	24	Trace

Temperature						
12	10	K ₂ CO ₃	DMF	60	24	40
13	10	K ₂ CO ₃	DMF	90	12	75 ^[c]

^[a] Reaction conditions: 4-iodonitrobenzene (0.5 mmol), phenylacetylene (0.6 mmol), Base (2 mmol), Solvent (4 mL), N₂ atm^[b] Isolated yield ^[c] in air

Considering the optimized condition from Table 1, the activity of Cu-463K was studied for Sonogashira coupling of electronically diverse aryl iodides and phenylacetylene (Table 2). The reaction provides excellent conversion for *para*- and *meta*- substituted electron withdrawing aryl iodides (Table 2, entries 1-8). However, catalytic activity seems to be moderate for 4-bromoiodobenzene (Table 2, entry 3). This may due to the contribution of positive resonance effect (+R) of the bromo substituent which increases the electron density over phenyl ring and causes difficulty in C-I bond breaking. Again, it is observed that electron donating aryl iodides are less competent than electron withdrawing species (Table 2, entry 4). Next, the effect of different substituted phenylacetylene was studied and no such significant difference in yield and duration on the cross-coupling reaction was observed (Table 2, entries 7 and 8). It was found that coupling of 3-iodobenzaldehyde and 3-methylphenylacetylene resulted in poor conversion. Additionally, lower conversion of desired product was obtained in case of disubstituted electron donating aryl iodide (Table 2, entry 10). Again, the coupling of heteroaryl iodide for example, 3-iodopyridine was investigated, and a moderate yield of cross-coupling product was obtained (Table 2, entry 11).

Table 2. Sonogashira cross-coupling of aryl iodides and phenylacetylene ^[a]

Entry	R ¹	R ²	Time(h)	Yield (%) ^[b]
1	4-NO ₂	C ₆ H ₅	12	90
2	4-COMe	C ₆ H ₅	12	91
3	4-Br	C ₆ H ₅	24	70
4	4-OMe	C ₆ H ₅	24	80
5	3-NO ₂	C ₆ H ₅	12	85
6	3-CHO	C ₆ H ₅	24	80
7	4-NO ₂	4-MeC ₆ H ₅	12	90
8	4-COMe	3-MeC ₆ H ₅	24	80
9	3-CHO	3-MeC ₆ H ₅	24	40
10	2,6-CH ₃	C ₆ H ₅	24	40
11	3-Iodopyridine	C ₆ H ₅	12	60

^[a] Reaction conditions: aryl iodide (0.5 mmol), phenylacetylene (0.6 mmol), Cu-463K (10 wt%), K₂CO₃ (2 mmol), DMF (4 mL), N₂ atm; ^[b] Isolated yield

Next, the catalytic efficiency of the Cu/Cu₂O NPs (Cu-463K) was examined towards C-N cross-coupling of aryl boronic acids and imidazoles.

In order to get the optimized condition for the reaction, phenyl boronic acid and imidazole were

chosen as model substrates, in the presence of CH₃OH at 60 °C. A set of reactions were performed to investigate the amount of the catalyst required for the transformation (Table 3, entries 1-3). It was observed that the reaction affords effective coupling with 20 wt% of Cu-463K (Table 3, entry 3). However, lower yields were obtained with 15 wt% and 10 wt%, owing to incomplete conversion of reaction substrates (Table 3, entries 1&2). This was further followed by investigating the amount of substrates required for the reaction. The appropriate ratio of the substrates was determined by carrying out test reactions choosing different equivalent ratios (Table 3, entries 4-6). The best result of cross-coupling was achieved with 1:1.2 equivalents of arylboronic acid and imidazole respectively (Table 3, entry 4). Since the medium under which the reaction was performed, determines the catalytic efficiency, we next investigated the effect of different solvents on the present catalytic system (Table 3, entries 7-10). However, among them, a greater yield of *N*-arylimidazole was obtained only with MeOH (Table 3, entry 2 vs entries 7-10). Additionally, the reaction was also performed under room temperature, but no conversion of the desired product was noticed (Table 3, entry 11). The optimized condition will be employed in the substrate study of C-N cross-coupling of aryl boronic acids and imidazoles.

Table 3. Optimization of a catalytic system for C-N cross-coupling reaction ^[a]

c1ccc(cc1)B(O)O + C1=CN=CN1
 $\xrightarrow[\text{Solvent}]{\text{Cu-463K}}$
c1ccc(cc1)N1=CN=C1

A
B

Entry	Cu-463K (wt%)		Solvent (mL)	Time (h)	Yield (%) ^[b]
Catalyst loading					
1	10		MeOH	10	55
2	15		MeOH	7	85
3	20		MeOH	7	90
Substrate ratio					
4	A (1)	B(1.2)	MeOH	7	90
5	A (1)	B(1.5)	MeOH	7	85
6	A (1)	B(1)	MeOH	9	82
Solvent effect					
7	20		H ₂ O	8	60
8	20		2-MeTHF	10	nr
9	20		H ₂ O:MeOH (1:1)	7	55
10	20		DMF	10	30
11	20		MeOH (r.t)	10	nr

^[a] Phenyl boronic acid (0.5 mmol), Imidazole (0.6 mmol), Solvent (4 mL), 60 °C ^[b] Isolated yield

The Chan-Lam reaction is extended to various arylboronic acids and imidazole derivatives (This work is published in *Catalysis Letters* (2023) 153:1423–1437)

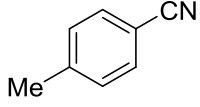
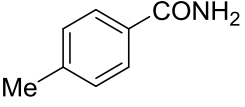
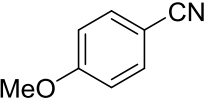
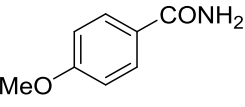
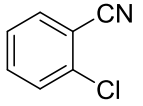
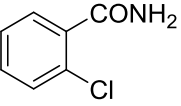
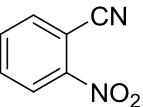
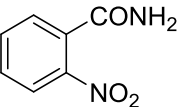
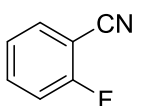
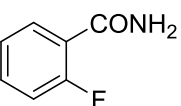
Another green and environmentally favorable methodology was developed for the hydration of aromatic nitriles to amides using 30% aqueous H₂O₂ employing an agricultural waste derived ‘water extract of banana peel ash’ (WEB) as the reaction medium without the aid of an external base. The extract exhibited dual functionality of acting as a base and a medium for the reaction. The pure products were isolated by simple filtration and involved no

complex chromatographic separations and purifications.

With the optimized condition, different electronically diverse aromatic nitriles were examined (Table 4, entries 1-11). For some of the substrates, on monitoring the progress of the reaction by TLC, it was found that 2 mL of H₂O₂ was necessary for smooth completion of the reaction (Table 4, entries 6-11). Aromatic nitriles with both electron donating and electron withdrawing groups were well susceptible to the current methodology. The *m*- and *p*-substituted nitriles were well tolerable by the method and gave the corresponding amides in excellent yields (Table 4, entries 2-8). However, the *o*-substituted nitriles exhibited a relatively lower rate of reaction (Table 4, entries 9-11). However, no over-hydrolysis of nitriles to acid was observed for the current protocol which makes it a versatile method for hydration of nitriles to amides.²

Table 4. WEB-30 % aq. H₂O₂ promoted hydration of nitriles^a

Entry	Substrate	Product	30% aq.H ₂ O ₂ (mL)	Time (h)	Yield ^b (%)
1			1	1	94
2 ^c			1	2	97
3 ^c			1	1	95
4			1	1	95
5 ^c			1	6	84
6			2	3.5	94

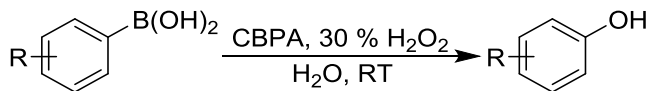
7 ^c			2	4	96
8 ^c			2	3.5	86
9 ^c			2	7	88
10			2	4.5	90
11			2	2	70

^aReaction conditions: Substrate (1 mmol), H₂O₂ (1 mL), WEB (3 mL) at 60 °C unless otherwise mentioned, ^bIsolated yield, ^c 0.5 mL of 2-Me THF was added to enhance solubility, ^d1 mL of EtOH was added to enhance solubility as it was not soluble in 2-MeTHF.

The protocol proceeds in the natural feedstock WEB avoiding the addition of an external base and do not demand any toxic and volatile organic solvents. The work was published in *Current Research in Green and Sustainable Chemistry*, 2021, 4, 100071.

Focusing on the utilisation of agro-wastes, we have also developed a reaction protocol for *ipso*-hydroxylation of arylboronic acids utilising a sustainable heterogeneous agro-waste based catalyst Calcined Burnt Peel Ash (CBPA) of the *Musa balbisiana Colla*. The catalyst CBPA was prepared and characterised by following a reported procedure.^{2,3} For the preparation of the catalyst, 50 g of ripe banana peels (*Musa balbisiana Colla*) were collected, cut into pieces, washed with double distilled water thrice and dried in oven for 48 h at 80 °C. After drying, the banana peels were burnt in open air to produce ash which was finally milled to powder. The powder, thus obtained, was sieved to fine ash and the sieved ash was calcined in a muffle furnace at 700 °C for 4 h in order to obtain calcined burnt peel ash (CBPA). The characterisations of CBPA are carried out as per previously reported method and confirmed.^{2,3} Various techniques used for characterisation reveal the higher basicity of CBPA. The p-XRD pattern explained the presence of a complex mixture of potassium and calcium compounds in the form of carbonates, oxides, silicates and sulphides in CBPA.³ The EDX analyses of the catalyst depicted the presence of compounds of K, Ca and Mg and Na and FTIR exhibited the presence of Ca and K species.³ The combined effect of presence of these species generates more basic sites in CBPA which make it a more promising basic heterogeneous catalyst.³

The use of 10 wt % CBPA along with 0.5 mL 30 % H₂O₂ in 2 mL of H₂O was finalized as the optimized reaction condition (Scheme 3).



Scheme 3. Bio-based catalysis for *ipso*-hydroxylation of boronic acids.

The heteroarylboronic acids were also compatible with the present reaction conditions with very good yields. The reaction yields proved that the current protocol is effective for both the electron-donating as well as the electron-withdrawing functional group containing arylboronic acid moieties. The used heterogeneous catalyst CBPA had shown excellent capability of reuse up to 5th cycle without significant loss in the reaction yield for the model reaction.

Use of bio-based reusable heterogeneous catalyst, short reaction time, water as solvent, metal free and ligand free mild reaction conditions makes the current protocol an attractive alternative for *ipso*-hydroxylation reaction. The work was published in *Sustainable Chemistry and Pharmacy*, 2020, 17, 100296.

In an another work the application of a cheap biocatalyst, Baker's Yeast, have been used as heterogeneous catalyst towards quick, water mediated, chemoselective, oxidative hydroxylation of aryl/heteroarylboronic acids and arylboronate esters at room temperature, in a metal and ligand free condition, without the addition of external base or acid. This work is published in *Sustainable Chemistry and Pharmacy* 19 (2021) 100363

10. Detailed analysis of results indicating contributions made towards increasing the state of knowledge in the subject:

The present methodology highlights an economical alternative strategy for the synthesis of copper NPs using agro-waste material. The *in situ* fabrication of Cu₂O particles on the Cu surface *via* gas phase H₂O/O₂ stimulation without the assistance of conventional reducing agents opens up a newer perspective for the generation of metal NPs. The synergistic action between the biphasic Cu(0) and Cu(I) surface shows preliminary activity in palladium free-Sonogashira cross coupling reaction. Moreover, as future scope, this synthetic methodology can be extended to the synthesis of tri-phasic Cu/Cu₂O/CuO NPs or bi/trimetallic heterogeneous catalytic system, which might be effective in different catalytic organic transformations. On the other hand, a facile methodology for the hydration of nitriles using a green alkaline extract WEB and 30% aqueous H₂O₂ paved a way for avoiding the addition of an external base and toxic/volatile organic solvents. The methodology does not involve any laborious separation or purification techniques and over hydrolysis to acid was also controlled. Thus, the protocol has the potential to work as an alternative green route for hydration of nitriles to amides using aqueous H₂O₂. Moreover a biobased heterogeneous catalyst is developed for *ipso*-hydroxylation of arylboronic acids for the synthesis of phenols.

11. Conclusions summarising the achievements and indication of scope for future work:

- i) Green methodology is developed for the synthesis of Cu nanoparticles. The synthesized nanoparticles are effectively used for C-C and C-N bond formation reactions.
- ii) Biobased green heterogeneous catalyst has been developed for hydration of nitriles
- iii) Biobased green reusable catalyst is developed for *ipso*-hydroxylation reaction.

All the developed methods are very efficient and green and these has huge potential for further scale up for the industrial utilization. There catalyst can also be explored for other industrially relevant reactions.

12. S&T benefits accrued:

i. List of Research publications

S No	Authors	Title of paper	Name of the Journal	Volume	Pages	Year	IF
1	Das, S. K., Tahu, M., Gohain, M. Deka, D, Bora, U	<i>Bio-based sustainable heterogeneous catalyst for ipso-hydroxylation of arylboronic acid,</i>	<i>Sustainable Chemistry and Pharmacy, ,</i>	17	100296	2020	5.464
2	Das, S. K.; Bhattacharje, P.; Sarmah, M.; Kakati, M.; Bora, U	A sustainable approach for hydration of nitriles to amides utilising WEB as reaction medium,	<i>Curr Res Green Sustain Chem,</i>	4	100071	2021	-
3	Mahanta, M., Dutta, A., Thakur, A. J., Bora, U.,	<i>Biocatalysis with Baker's Yeast: A green and sustainable approach for C-B bond cleavage of aryl/heteroarylboronic acid and boronate esters at room temperature</i>	<i>Sustainable Chemistry and Pharmacy</i>	19	100363	2021	5.464
4	Sarmah, M.; Sarmah. D.; Dewan, A.; Bora, P.; Boruah, P. K.; Das, M. R.; Bharali, P.; Bora, U.	<i>Dual Responsive Sustainable Cu₂O/Cu Nanocatalyst for Sonogashira and Chan-Lam Cross-Coupling Reactions, ,</i>	<i>Catalysis Letters</i>	153	1423– 1437	2023	2.936

ii. Manpower trained on the project

- Research Scientists or Research Associates : Two postdoctoral fellows
- No. of Ph.D. produced: 02
- Other Technical Personnel trained: 05 (M.Sc. project)

iii. Patents taken, if any: Nil

13. Financial Position:

No	Financial Position/ Budget Head	Funds Sanctioned	Expenditure	% of Total cost
I	Salaries/ Manpower costs	Nil		
II	Equipment	Nil		
III	Supplies & Materials	Nil		
IV	Contingencies	50,000/-	50,000/-	100%
V	Travel	200000/-	Nil	No exchange visit from both Indian & Bulgarian side could be carried out due to COVID-19 outbreak
VI	Overhead Expenses	38675/-	38675/-	100%
VII	Others, if any	302500/-	Nil	No exchange visit from both Indian & Bulgarian side could be carried out due to COVID-19 outbreak
	Total	591175/-	88675/-	15%

14. Procurement/ Usage of Equipment : No equipment purchased under this project

a)

S No	Name of Equipment	Make/Model	Cost (FE/Rs)	Date of Installation	Utilisation Rate (%)	Remarks regarding maintenance/breakdown

b) Plans for utilizing the equipment facilities in future: No equipment purchased under this project

15. Exchange visits undertaken: No exchange visit have undertaken due to COVID 19 outbreak

a) India to Partner Country

S No	Name of Scientist	Institutions visited	Duration	Remarks if any

a) Partner Country to India

S No	Name of Scientist	Institutions visited	Duration	Remarks if any

Name and Signature with Date

Utpal Bora
3/7/23
a. Dr. Utpal Bora, Principal Investigator

Pankaj Bharali
03/07/2023
b. Dr Pankaj Bharali, Co-Investigator

GFR 12 – A

[(SEE RULE 238 (1)]

FORM OF UTILIZATION CERTIFICATE FOR THE GRANTEE ORGANIZATION INCLUDING AUTONOMOUS ORGANIZATIONS

UTILIZATION CERTIFICATE FOR THE YEAR **2022-23**
(period ending **18th September 2022**)
In respect of **recurring/non-recurring**
GRANT-IN-AID/SALARIES/CREATION OF CAPITAL ASSETS

1.	Name of the scheme: <i>Green and sustainable catalysts based on zeolites for oxidative transformation reactions</i> (Sanctioned under India-Bulgaria Bilateral Scientific & technological Cooperation)
2.	Whether recurring or non-recurring grants: Recurring
3.	Grants position at the beginning of the financial year
	(i) Cash in Hand/Bank: 502500/- (ii) Unadjusted advances: Nil (iii) Total: 502500/-

4. Details of grants received, expenditure incurred and closing balances: (Actuals)

Unspent Balances of Grants received year [figure as at SI No 3(iii)]	Interest earned thereon	Interest deposited back to the government	Grant received during the year 2021-22			Total Available funds (1+2-3+4)	Expenditure incurred	Closing Balance (5-6)
			Sanction no. (i)	Date (ii)	Amount (iii)			
1	2	3	4			5	6	7
502500/-	9422/-	9422/- (Bharatokosh ReceiptNo:0302230004934)	DST/INT/BLR /P-15/2019	18.9.2019	Nil	502500/-	Nil	502500

5. Component wise utilization of grants:

Grants-in-aid-General	Grant-in-aid -Salary	Grants-in-aid-creation of capital	Total
Nil	Nil	Nil	Nil

6. Details of grants position at end of the year

- (i) Cash in Hand /Bank: 502500/-
(ii) Unadjusted Advance: Nil
(iii) Total: 502500/-

7. Certified that I have satisfied myself that the conditions on which grants were sanctioned have been duly fulfilled /are being fulfilled and that I have exercised following checks to see that the money has been actually utilized for the purpose for which it was sanctioned:

- (i) The main accounts and other subsidiary accounts and registers (including assets register) are maintained as prescribed in the relevant Act/Rules/standing instructions (mention the Act/Rules) and have been duly

audited by designated auditors. The figures depicted above tally with the audited figures mentioned in financial statements/accounts.

- (ii) There exist internal controls for safeguarding public funds/assets, watching outcomes and achievements of physical targets against the financial inputs, ensuring quality in asset creation etc. & the periodic evaluation of internal controls is exercised to ensure their effectiveness.
- (iii) To the best of our knowledge and belief, no transactions have been entered that are in violation of relevant Act/Rules/standing instructions and scheme guidelines.
- (iv) The responsibilities among the key functionaries for execution of the scheme have been assigned in clear terms and are not general in nature.
- (v) The benefits were extended to the intended beneficiaries and only such areas/districts were covered where the scheme was intended to operate.
- (vi) The expenditure on various components of the scheme was in the proportions authorized as per the scheme guidelines and terms and conditions of the grants-in-aid.
- (vii) It has been ensured that the physical and financial performance under.....(name of the scheme has been according to the requirements, as prescribed in the guidelines issued by Govt. of India and the performance/targets achieved statement for the year to which the utilization of the fund resulted in outcomes give at Annexure- I duly enclosed.
- (viii) The utilization of the fund resulted in outcomes given at Annexure – II duly enclosed (to be formulated by the Ministry /Department concerned as per their requirements/specifications.)
- (ix) Details of various schemes executed by the agency through grants-in-aid received from the same Ministry or from other Ministries is enclosed at Annexure—II (to be formulated by the Ministry/Department concerned as per their requirements/specifications).

Date:

Place: Tezpur

Signature

Name

Chief Finance Officer
(Head of the Finance)

*Finance Officer
Tezpur University*

Signature

Name

Head of the Organisation

*Registrar
Tezpur University*

(TO BE FILLED IN BY DST)

2. Certified that I have satisfied myself that the conditions on which the grants-in-aid was sanctioned have been fulfilled/are being fulfilled and that I have exercised the following checks to see that the money was actually utilised for the purpose for which it was sanctioned:

Kinds of checks exercised.

- 1.
- 2.
- 3.
- 4.
- 5.

Signature
Designation
Date

**REQUEST FOR ANNUAL INSTALLMENT WITH
UP-TO-DATE STATEMENT OF EXPENDITURE**

(Year Means Financial Year 1st April 2019 to 31st March of 2020)

1. Sanction Letter No. DST/INT/BLR/P-15/2019	6. Grant Received in each year:
2. Total Project Cost Rs. 1182350/-	a. I year Rs. 591175/-
3. Sanctioned/Revised project cost (if applicable): Rs. 1182350/-	b. II-year Rs. Nil
4. Date of commencement of Project: 18/9/2019	c. III-year Rs. Nil
5. Statement of Expenditure	d. Interest Rs. 8163/- (1 st) + 5941 (2 nd) + 12563/- (3 rd) + 9422/- (4 th) (Interests are returned to Bharatkosh) if any
	e. Total Rs. 591175/-

Month & Year	Expenditure incurred/ committed
1 st April 2021 to 18 th September 2022	Nil

Note:

1. Expenditure under the sanctioned heads, at any point of time, should not exceed funds allocated under the head, without prior approval of DST i.e. Figures in Column (vii) should not exceed corresponding figures in Column (iii)
2. Utilisation Certificate for each financial year ending 31st March has to be enclosed, along with request for carry-forward permission to next year

Annexure IInd Continued

SI. No.	Sanctioned Heads**	Funds Allocated (*)	Expenditure Incurred					Balance as on date (Col. iii - vii)	Required Funds till 31 March 2023	Remarks (if any)
			I Yr.	II Yr.	III Yr.	IV Yr.	Total (iv+v+vi)			
i.	ii.	iii.	iv.	v.	vi.		vii.	viii.	ix.	x.
1.	Salaries	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	
2.	Permanent Equipments	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	
3.	Supplies & Materials/consumables	Nil	Nil	Nil	Nil	Nil	Nil	Nil	Nil	
4.	Travel of Indian Scientists Abroad	200000/-	Nil	Nil	Nil	Nil	Nil	200000/-	Nil	No exchange visit from Indian and Bulgarian side could be carried out due to worldwide COVID-19 outbreak during this period
5.	Hospitality of Foreign Scientists Per diem @ 2500*21 days =52500 And 50000*03 months = 150000 Rs. 100000 - Accommodation	52500/- 150000/- 100000/-	Nil	Nil	Nil	Nil	Nil	52500/- 150000/- 100000/-	Nil	
6.	Contingencies	50000/-	Nil	49244/-	756	Nil	50000/-	Nil	Nil	
7.	Overhead Expenses	38675/-	Nil	25672/-	13003	Nil	38675	Nil	Nil	
8.	Interest earned	8163 + 5914 +12563+ 9422	-	-	Nil	Nil	-	-	Nil	Refund to the Bharatkosh
	Total	591175/-		74916/-	13759	Nil	88675	502500/-	Nil	

Note : * Please indicate heads and allocation as per original / revised (if any) sanction order approving/ revising the project

Name & Signature

Principal Investigator: Dr Utpal Bora

Date: 9.2.23

Signature of Competent financial authority

Date:

Finance Officer
Tezpur University