FORM-F

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH
Human Resource Development Group
(Extra Mural Research Division)
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

PROFORMA FOR PREPARING FINAL TECHNICAL REPORT
(Five copies of the report must be submitted immediately after completion of the research scheme)

1. Title of the scheme

Design of Zeolite-Y Supported Heterogeneous Catalyst For C-C Bond Coupling Reactions	Scheme No.: **80(0094)/20/EMR-II**, Date of Commencement: **01/10/2020** Date of termination: **30/09/2024**

2. Name and address of Principal Investigator

Prof. Kusum K. Bania
Department of Chemical Sciences,
Tezpur University, Napaam, Assam 784028, India

3. Name of Sponsoring laboratory of CSIR (If applicable)

Indian Institute of Chemical Technology, Uppal Road, Tarnaka, Hyderabad, Telangana 500007, India

4. Total grant sanctioned and expenditure during the entire tenure

	Amount Sanctioned (in Rs)				**Expenditure (in Rs)**			
	FY 2020-2021	**FY 2021-2022**	**FY 2022-2023**	**FY 2023-2024**	**FY 2020-2021**	**FY 2021-2022**	**FY 2022-2023**	**FY 2023-2024**
Staff	217000	226000	390000	444000	71000	373000	390000	444000
Contingency	145833	Rs. 41667 + Rs.421 (from previous	Rs. 62479 + Rs.423 (from	250000 + Rs. 23 (from previous	144412	41665	62879	250023

		year) =42088	previous year) = 62902	year) =250023				
Equipment	500000	NIL (*Rs. 58644 Returned)*	NIL	NIL	441356	NIL	NIL	NIL
Total	862833	268088	452902	694023	656768	414665	452897	694023

5. Equipment(s) purchased out of CSIR grant

Name	Cost
Rotary Evaporator	**Rs. 4,41,356/-**

6. Research fellows associated with scheme

Name & Designation	Date of Joining	Date of leaving
Mr. Subir Biswas, JRF	**23/12/2020**	**31/03/2024**

7. Name(s) of the fellow(s) who received Ph.D. by working in the scheme, along with the Title(s) of thesis:

(i) Subir Biswas

Thesis title: Zeolite-Y Supported Nanocatalysts for C-C Bond Formation Reactions.

8. List of research papers published/communicated, based on the research work done under the scheme (Name(s) of author(s), Title, Journal, Volume number, Year and Pages should be given for each paper published and a copy of each of them should be enclosed; reprints/copies of papers appearing after submission of FTR should also be sent to CSIR):

(i) Bora, Tonmoy J., Nand K. Gour, Lakshi Saikia, Unnati Bora, Nitumoni Hazarika, Donguk Kim, Young-Bin Park et al. "Highly dispersed Pd-nanoparticles in vanadium oxide supported zeolite-Y for CC coupling reaction through C-Cl bond activation." *Applied Catalysis A: General* 691 (2025): 120053. (https://doi.org/10.1016/j.apcata.2024.120053) **IF: 4.7**

(ii) Biswas, Subir, Dipankar Barman, Priyanka Dutta, Nand K. Gour, Seonghwan Lee, Donguk Kim, Young-Bin Park et al. "Ru-nanoparticles supported on zeolite-Y for ortho-benzylation of phenols and activation of H 2 O 2 for selective synthesis of BINOLs." *Catalysis Science & Technology* 14, no. 18 (2024): 5234-5256. (https://doi.org/10.1039/D4CY00429A) **IF: 4.4**

(iii) Devi, Arpita, Mrinmoy Manash Bharali, Seonghwan Lee, Young-Bin Park, Lakshi Saikia, Rafikul Ali Saha, Tanmoy Kalita et al. "Photoactivation of peroxymonosulfate (PMS) over a CuO–ZnO p–n heterojunction for the selective C2 trimerization of indoles." *Catalysis Science & Technology* 14, no. 9 (2024): 2400-2415. (https://doi.org/10.1039/D4CY00067F) **IF: 4.4**

(iv) Saikia, Sayanika, Lakshi Saikia, Seonghwan Lee, Young-Bin Park, Rafikul Ali Saha, Salma A. Khanam, Magdi EA Zaki, and Kusum K. Bania. "Cu (I/II)-Co (II/III) photocatalyst with intrinsic electron transport centre for photoreduction of chromium (VI) and photodegradation of methyl violet." *Journal of Environmental Chemical Engineering* 12, no. 2 (2024): 112344.. (https://doi.org/10.1016/j.jece.2024.112344) **IF: 7.4**

(v) Khanam, Salma A., Sayanika Saikia, Seonghwan Lee, Young-Bin Park, Magdi EA Zaki, and Kusum K. Bania. "Interfacial Effect-Induced Electrocatalytic Activity of Spinel Cobalt Oxide in Methanol Oxidation Reaction." *ACS omega* 8, no. 47 (2023): 44964-44976. (https://doi.org/10.1021/acsomega.3c06414) **IF: 3.7**

(vi) Gogoi, Gautam, Nand K. Gaur, Seonghwan Lee, Young-Bin Park, Lakshi Saikia, Magdi EA Zaki, and Kusum K. Bania. "Copper oxide in layered tin oxide with intracrystalline microporosity for oxidative imination of toluene and p-xylene." *Molecular Catalysis* 550 (2023): 113534. (https://doi.org/10.1016/j.mcat.2023.113534) **IF: 3.9**

(vii) Saikia, Sayanika, Manoshi Saikia, Salma A. Khanam, Seonghwan Lee, Young-Bin Park, Lakshi Saikia, Gautam Gogoi, and Kusum K. Bania. "Cobalt oxide decked with inorganic-sulfur containing vanadium oxide for chromium (vi) reduction and UV-light-assisted methyl orange degradation." *Materials Advances* 4, no. 23 (2023): 6244-6258. (https://doi.org/10.1039/D3MA00625E) **IF: 5.2**

(viii) Bora, Tonmoy J., Nitumoni Hazarika, Nand K. Gour, Seonghwan Lee, Young-Bin Park, Subir Biswas, Arpita Devi, and Kusum K. Bania. "Low-Palladium-Content Iron (III) Nanocatalyst Supported on Zeolite-NaY for C–Cl Bond Activation." *ACS Applied Nano Materials* 6, no. 19 (2023): 17972-17985. (https://doi.org/10.1021/acsanm.3c03244) **IF: 5.3**

(ix) Hoque, Nazimul, Seonghwan Lee, Young-Bin Park, Subhasish Roy, Magdi EA Zaki, and Kusum K. Bania. "Ni (OH) 2-SnO2 at the hybrid interface of zeolite-Y and rGO for electrochemical oxidation of methanol and ethanol." *Energy & Fuels* 37, no. 15 (2023): 11309-11318. (https://pubs.acs.org/doi/10.1021/acs.energyfuels.3c01521) **IF: 5.2**

(x) Gogoi, Gautam, Sayanika Saikia, Abhijit Das, Simashree Saikia, Nazimul Hoque, Subir Biswas, Mrityunjoy Dey, Pabitra Kumar Kalita, and Kusum K. Bania. "Iron and copper catalysts derived from inorganic waste for dye degradation." *ChemistrySelect* 8, no. 27 (2023): e202300279. (https://doi.org/10.1002/slct.202300279) **IF: 1.9**

(xi) Devi, Arpita, Mrinmoy Manash Bharali, Subir Biswas, Tonmoy J. Bora, Jayanta K. Nath, Seonghwan Lee, Young-Bin Park, Lakshi Saikia, Manash J. Baruah, and Kusum K. Bania. "Utilization of methanol and ethanol for 3, 3'-bis (indolyl) methane synthesis through activation of peroxymonosulfate over a copper catalyst." *Green Chemistry* 25, no. 9 (2023): 3443-3448. (https://doi.org/10.1039/D3GC00440F) **IF: 9.3**

(xii) Biswas, Subir, Dipankar Barman, Gautam Gogoi, Nazimul Hoque, Arpita Devi, Siddhartha K. Purkayastha, Ankur Kanti Guha, Jayanta K. Nath, and Kusum K. Bania. "Heterogeneous iron catalyst for C (1)–H functionalization of 2-naphthols with primary aromatic alcohols." *Organic & Biomolecular Chemistry,* 21, (2023): 1657-1661. (https://doi.org/10.1039/D3OB00004D) **IF: 2.9**

(xiii) Khanam, Salma. A., Nazimul Hoque, Seonghwan Lee, Young-Bin Park, Gautam Gogoi, and Kusum K. Bania. "Tubular nickel hydroxide embedded in zeolitic cobalt oxide for methanol oxidation

reaction." *ACS Applied Energy Materials*, 5 (2022): 12651-12662. (https://doi.org/10.1021/acsaem.2c02286) **IF: 5.5**

(xiv) Gogoi, Gautam, Jayanta K. Nath, Nazimul Hoque, Subir Biswas, Nand K. Gour, Dhruba Jyoti Kalita, Smiti Rani Bora, and Kusum K. Bania. "Single and Multiple Site Cu (II) Catalysts for Benzyl Alcohol and Catechol Oxidation Reactions."*Applied Catalysis A: General* 644 (2022): 118816. (https://doi.org/10.1016/j.apcata.2022.118816) **IF: 4.7**

(xv) Gogoi, Gautam, Manash J. Baruah, Subir Biswas, Nazimul Hoque, Seonghwan Lee, Young-Bin Park, Lakshi Saikia, and Kusum K. Bania. "CuO-Fe (III)-Zeolite-Y as efficient catalyst for oxidative alcohol-amine coupling reactions."*Molecular Catalysis* 528 (2022): 112458. (https://doi.org/10.1016/j.mcat.2022.112458) **IF: 3.9**

(xvi) Hoque, Nazimul, Seonghwan Lee, Young-Bin Park, Subhasish Roy, Manash J. Baruah, Subir Biswas, Gautam Gogoi, Tonmoy J. Bora, Rupjyoti Dutta, and Kusum kumar Bania. "Dual Matrix Influence on Ni (II) Rich Hybrid Catalyst for Electrochemical Methanol Oxidation Reaction."*ChemNanoMat* (2022): e202200280. (https://doi.org/10.1002/cnma.202200280). **IF: 2.6**

(xvii) Hoque, Nazimul, Manash J. Baruah, Arif Hassan Biman, Subir Biswas, Gautam Gogoi, Rupjyoti Dutta, and Kusum K. Bania. "Impregnating Rhodium (0) Sites through Zeolite-Y Templation in a Hybrid Rh–Ni Catalyst for Alcohol Electro-Oxidation with Low CO Poisoning." *ACS Applied Energy Materials* 5 (2022): 6118–6128. (https://doi.org/10.1021/acsaem.2c00523) **IF: 5.5**

(xviii) Biswas, Subir, Manash J. Baruah, Gautam Gogoi, Nazimul Hoque, Seonghwan Lee, Young-Bin Park, Lakshi Saikia, and Kusum K.Bania. "Dehydrogenation of ethanol over CuO–Mg–Y for cross-aldol condensation with aryl aldehydes." *Microporous and Mesoporous Materials* (2022): 111893. (https://doi.org/10.1016/j.micromeso.2022.111893) **IF: 4.8**

(xix) Baruah, Manash J., Anurag Dutta, Subir Biswas, Gautam Gogoi, Nazimul Hoque, Pradip K. Bhattacharyya and Kusum K. Bania. "Fe_2O_3 Nanocatalysts Supported on Zeolite-Y for the Selective Synthesis of C2 Di-Indolyl Indolones and Isatins." *ACS Applied Nano Materials*, 5 (2022): 1446-1459. (https://doi.org/10.1021/acsanm.1c03987) **IF: 5.3**

(xx) Baruah, Manash J., Tonmoy J. Bora, Gautam Gogoi, Nazimul Hoque, Nand K. Gour, Suresh K. Bhargava, Ankur K. Guha, Jayanta K. Nath, Biraj Das, and Kusum K. Bania. "Chirally modified cobalt-vanadate grafted on battery waste derived layered reduced graphene oxide for enantioselective photooxidation of 2-naphthol: Asymmetric induction through non-covalent interaction." *Journal of Colloid and Interface Science* 608 (2022): 1526-1542. (https://doi.org/10.1016/j.jcis.2021.10.091) **IF: 9.4**

(xxi) Hoque, Nazimul, Manash J. Baruah, Seonghwan Lee, Young-Bin Park, Rupjyoti Dutta, Subhasish Roy, and Kusum K. Bania. "Cu $(OH)_2$-Ni $(OH)_2$ engulfed by zeolite-Y hydroxyl nest and multiwalled carbon nanotube for effective methanol oxidation reaction." *Electrochimica Acta* 397 (2021): 139313. (https://doi.org/10.1016/j.electacta.2021.139313) **IF: 5.5**

(xxii) Baruah, Manash J., Tonmoy J. Bora, Rupjyoti Dutta, Subhasish Roy, Ankur Kanti Guha, and Kusum K. Bania. "Fe (III) superoxide radicals in halloysite nanotubes for visible-light-assisted benzyl alcohol oxidation and oxidative C-C coupling of 2-naphthol." *Molecular Catalysis* 515 (2021): 111858. (https://doi.org/10.1016/j.mcat.2021.111858) **IF: 3.9**

(xxiii) Gogoi, Gautam, Pinku Saikia, Manash J. Baruah, Seonghwan Lee, Young-Bin Park, Rupjyoti Dutta, and Kusum K. Bania. "Mixed valent copper oxide nanocatalyst on Zeolite-Y for mechanochemical oxidation, reduction and C–C bond formation reaction." *Microporous and Mesoporous Materials* 326 (2021): 111392. (https://doi.org/10.1016/j.micromeso.2021.111392) **IF: 4.8**

9. Details of new apparatus or equipment designed or constructed during the investigation: NA

10. The likely impact of the completed work on the scientific/technological potential in the country (this may be attached as Enclosure-I): Attached with the **Final Technical Report** as **Enclosure I**.

11. Is the research work done of some industrial or agricultural importance and whether patent(s) should be taken? Yes/No; if yes, what action has been/should be taken:

Our synthesized showed remarkable potential biological activity. Twelve C-2 quaternary indolinones derivatives showed as novel therapeutic scaffolds to combat *Providencia* spp. bacterial group of the Enterobacteriaceae family known to cause urinary tract infections. Three functionalized naphthol derivatives are found very active for pneumonia treatment. Biological tests of the synthesized molecules to fight against *Klebsiella pneumoniae* and MRSA (*Methicillin resistant Staphylococcus aureus*) are two major causative organisms of healthcare-related infections. The synthesized scaffolds like β-aryl enals and enones derivatives are major precursors of various industry-related molecules. As our research is an interdisciplinary one so our developed methodologies and compounds have tremendous significance in both industrial and agriculture sectors. As the research project will generate new knowledge (methodologies, tools, and techniques for researching), the project outputs will result in an improved understanding of the new drug design methodology for pneumonia treatment via C-H bond activation of phenolic compounds. Thus, improved effectiveness of the health sector and, welfare, and a better environment with sustainability are inevitable outcomes of this work.

12. How has the research work complemented the work of CSIR Laboratory that sponsored your scheme?

We thank the Indian Institute of Chemical Technology (IICT) Hyderabad and Dr. Galla V. Karunakar, Principal Scientist, IICT Hyderabad for sponsoring our scheme. Various technical discussions, as well as several analyses were done with Dr. Karunakar and group. Scheme related discussion and cooperation were accomplished and guided by the CSIR-Laboratory.

13.Detailed account of the work carried out in terms of the objective(s) of the project and how for they have been achieved; results and discussion should be presented in the manner of a scientific paper/project report in about 5000 words; and this should be submitted as Enclosure-II to this report:

Attached with the **Final Technical Report** as **Enclosure II**

14. An abstract of research achievements in about 200-500 words, suitable for publication.

The CSIR-sponsored scheme gives us this opportunity and providing the grant to showcase our potentiality to the field of carbon-carbon (C-C) bond formation reaction using heterogeneous catalysts. The C-C bond formation reactions have contributed significantly to the construction of numerous important molecules that have contributed in various dimensions. The processes provide valuable fundamental tools for accessing diverse scaffolds in modern organic synthesis. Indeed, in the field of C-C bond formation, the utilization of benign, green and cost-effective

reusable protocols has made to find the potentially active synthetic process for the same. Heterogeneous catalysts that are recyclable and can convert a chemical reaction with the same affinity as that of the homogeneous counterpart provide an economically viable path. The project work therefore focuses on different types of C-C bond formation reactions triggered by transition metal nanocatalysts supported mostly on zeolite-Y. Through this scheme, we comprise our recent breakthrough devoted to various C-C bond formation reactions performed by such heterogeneous catalysts including photocatalysts. The objectives and outcomes of the scheme are briefly documented in this final technical report. The scheme is based on developing various zeolite-Y supported reusable metal catalysts for superficial formation of various C-C bond formation reactions like Suzuki-Miyaura cross-coupling (SMCC) reactions, oxidation coupling reaction of naphthols, cross-aldol condensation reactions, Friedel-Crafts benzylation reactions and synthesis of C-2, C-3 trimerization of indoles. The various approaches and the mechanistic insights that are highlighted in this reports in the activation of C-Cl bond are expected to provide a new dimension in SMCC reactions. The zeolite-NaYsupported Pd/PdO-Fe_2O_3-Y catalyst and Pd/PdO-VO_x-Y_{CVS} appeared as potential catalysts for SMCC reactions. The chirally modified Co-V oxide nanocatalyst on reduced graphene oxide and understand their behavior in asymmetric photo-oxidation of 2-naphthol. A Ru-based nanocatalyst on zeolite-Y that was employed for selective synthesis of biaryl derivatives yield up to 94% in a very short period under peroxide environments. Several α, β-unsaturated carbonyl compounds *via* cross-aldol condensation process utilizing *in situ* generated of acetaldehyde from ethanol over copper oxide (CuO) nanocatalyst supported on Mg^{2+}-exchanged zeolite-Y (CuO-Mg-Y). The report also reveals the ability of Fe_2O_3-Y catalyst to dehydrogenate methanol (C1) and ethanol (C2) alcohols for the *in situ* generation of formaldehyde and acetaldehyde. It provides a green protocol for synthesizing biologically important molecules 3,3'-bis(indolyl)methanes derivatives. Subsequently, this scheme reveals for the first time the utilization of Fe_2O_3 nanocatalysts supported on potassium exchanged zeolite-Y (Fe_2O_3-KY) for the Friedel Crafts benzylation of naphthol and also the promising activity of Ru nanos on zeolite-Y for benzylation of phenol.

15. Mention here whether or not the unspent grant has been refunded to CSIR:
An amount of **Rs. 58644** remaining unutilized under equipment head at the end of the year has been surrendered to EMR, HRDG (CSIR) **(vide letter No. DD No: 535167 dated 01/06/2021)**

Date: 2.03.2022

Signature of PI

Note: Final Technical Report is expected to be self-contained complete report of the work done. Please do not leave any column unanswered.

Enclosure-I

10. Impact on the scientific/technological potential in the country

At the very onset, we thank CSIR for the grants. Our project designed and developed several heterogeneous, reusable metal nanocatalysts supported on zeolite-Y and various C-C bond formation reactions. We developed the utility of greener and inexpensive protocols using Fe_2O_3-Y in the synthesis of C2 trimerized products of indole. Which have the potential bioactivity of C-2 quaternary indolinones (molecule **1-12**) against *Providencia* spp., a bacterial group of the Enterobacteriaceae family known to cause urinary tract infections (**Figure 1A**). The experimental design and their unique structure make them novel therapeutic scaffolds to combat *Providencia* spp. Infections. Through this project we also breakthrough for the first time the ability of different catalysts to dehydrogenate C1 and C2 alcohols for the *in situ* generation of formaldehyde and acetaldehyde. Thereby it provides a green protocol for synthesizing important scaffolds like β-aryl enals, enones derivatives, and 3,3'-bis(indolyl)methanes. The same catalyst with potassium-exchanged zeolite-Y (Fe_2O_3-KY), appeared as an efficient reusable catalyst to promote the selective C(1)-H functionalization of 2-naphthol derivatives with various aromatic primary alcohols. We have successfully synthesized 26 benzylated naphthol derivatives, out of them the three compounds are found very active for pneumonia treatment (**Figure 1**). Biological test of the synthesized molecules (special attention for pneumoniae treatment): *Klebsiella pneumoniae* and MRSA (*Methicillin resistant Staphylococcus aureus*) are two major causative organisms of healthcare-related infections. Both are associated with significant morbidity and mortality. Even with newer generations of antibiotics, the threat posed by these two bacteria is prevalent. Benzylated 2-naphthol derivatives were developed to study the effects of these two MTCC strains. The compounds viz. **13-15** showed remarkable results against both *K. pneumoniae* and MRSA with greater zones of inhibition than that of the commercial antibiotic, Imipenem (**Figure 1**). Hence, we believe that by acquiring our synthetic procedures and methodology multiple beneficiaries within the commercial private sector, policy-makers (nationally and internationally), and local government agencies and regulators are all likely to benefit from the research outcome.

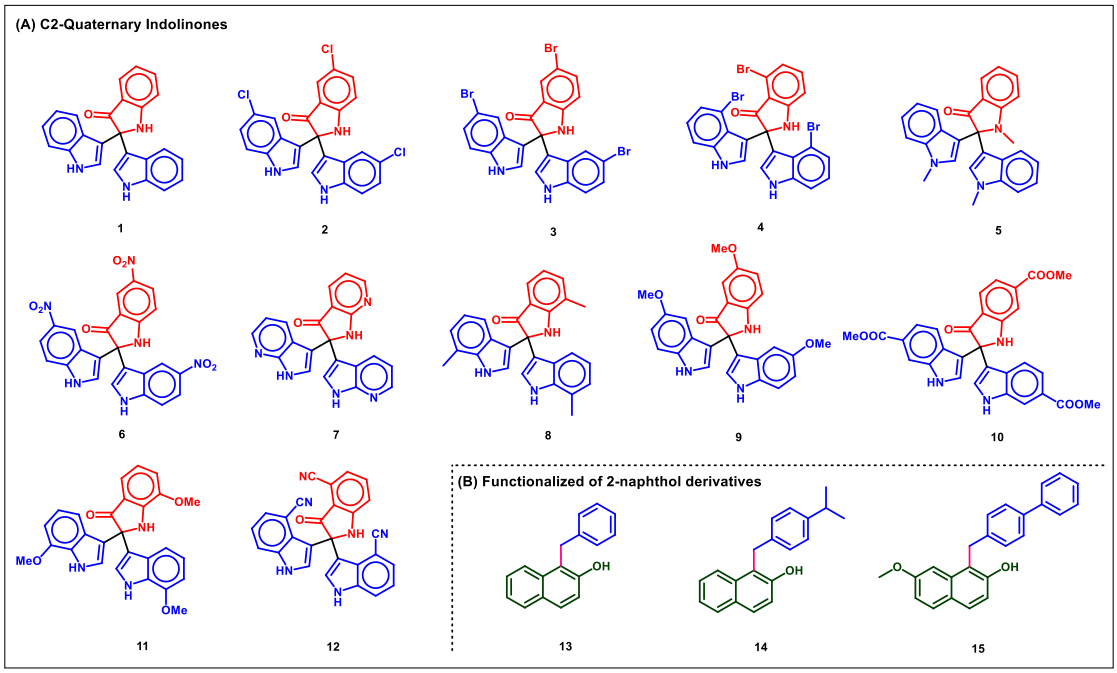


Figure 1. The relevant bio-active molecules from(A) C-2 quaternary derivatives, (B) 2-naphthol derivatives.

Enclosure-II

Scheme Title: Design of Zeolite-Y Supported Heterogeneous Catalyst for C-C Bond Coupling Reactions

Subir Biswas,[a] Kusum K Bania*[a]

[a]*Department of Chemical Sciences, Tezpur University, Assam 784028, India.* PI of the scheme.*

Abstract

The CSIR-sponsored scheme gives us this opportunity and providing the grant to showcase our potentiality to the field of carbon-carbon (C-C) bond formation reaction using heterogeneous catalysts. The C-C bond formation reactions have contributed significantly to the construction of numerous important molecules that have contributed in various dimensions. The processes provide valuable fundamental tools for accessing diverse scaffolds in modern organic synthesis. Indeed, in the field of C-C bond formation, the utilization of benign, green and cost-effective reusable protocols has made to find the potentially active synthetic process for the same. Heterogeneous catalysts that are recyclable and can convert a chemical reaction with the same affinity as that of the homogeneous counterpart provide an economically viable path. The project work therefore focuses on different types of C-C bond formation reactions triggered by transition metal nanocatalysts supported mostly on zeolite-Y. Through this scheme, we comprise our recent breakthrough devoted to various C-C bond formation reactions performed by such heterogeneous catalysts including photocatalysts. The objectives and outcomes of the scheme are briefly documented in this final technical report. The scheme is based on developing various zeolite-Y supported reusable metal catalysts for superficial formation of various C-C bond formation reactions like Suzuki-Miyaura cross-coupling (SMCC) reactions, oxidation coupling reaction of naphthols, cross-aldol condensation reactions, Friedel-Crafts benzylation reactions and synthesis of C-2, C-3 trimerization of indoles. The various approaches and the mechanistic insights that are highlighted in this reports in the activation of C-Cl bond are expected to provide a new dimension in SMCC reactions. The zeolite-NaYsupported Pd/PdO-Fe_2O_3-Y catalyst and Pd/PdO-VO_x-Y_{Cys} appeared as potential catalysts for SMCC reactions. The chirally modified Co-V oxide nanocatalyst on reduced graphene oxide and understand their behavior in asymmetric photo-oxidation of 2-naphthol. A Ru-based nanocatalyst on zeolite-Y that was employed for selective synthesis of biaryl derivatives yield up to 94% in a very short period under peroxide environments. Several α, β-unsaturated carbonyl compounds *via* cross-aldol condensation process utilizing *in situ* generated of acetaldehyde from ethanol over copper oxide (CuO) nanocatalyst supported on Mg^{2+}-exchanged zeolite-Y (CuO-Mg-Y). The report also reveals the ability of Fe_2O_3-Y catalyst to dehydrogenate methanol (C1) and ethanol (C2) alcohols for the *in situ* generation of formaldehyde and acetaldehyde. It provides a green protocol for synthesizing biologically important molecules 3,3'-bis(indolyl)methanes derivatives. Subsequently, this scheme reveals for the first time the utilization of Fe_2O_3 nanocatalysts supported on potassium exchanged zeolite-Y (Fe_2O_3-KY) for the Friedel Crafts benzylation of naphthol and also the promising activity of Ru nanos on zeolite-Y for benzylation of phenol.

1 Introduction

Zeolite-NaY is considered one of the host materials for trapping of small molecules and also provides highly selective in the reaction. zeolite-NaY with high surface area, good pore opening and supercage are known to be industrial catalysts as well as support for different metal catalysts.[5] Owing to its surface properties, Lewis acidity, and Brønsted acid-base sites, different metal cations can be exchanged to produce various metal-loaded zeolite-Y-based catalysts.[6] In addition to this different metal complexes can be encapsulated into the zeolite-NaY cavity and at the same time the zeolite-Y can serve as a matrix to support different metal nanocatalysts.[7] The presence of the surface hydroxyl

group introduces a suitable environment for anchoring different metal nanoparticles providing good surface-to-metal interactions. Along with this, the zeolite-NaY has a good surface area (600-700 m^2/g) and also prevents the agglomeration of the nanoparticles allowing their fine distribution on the surface. This in turn generates a higher number of active sites at the zeolite-Y surface of a similar nature and thereby increases the catalytic performances of the nanocatalyst. Zeolite-NaY not only helps in manipulating the nanoparticle dimension and their fine distribution but they can also alter the chemical properties of nanoparticles by changing the acidic or basic character. In recent years, our group has focused on designing various zeolite-Y encapsulated metal catalysts as well as the zeolite-Y supported nanocatalysts. This reports also summarized the activity of different metal catalysts on zeolite-Y for various carbon-carbon (C-C) bond formation reactions.

The C-C coupling of 2-naphthol to preferentially obtain the [1,1'-binaphthalene]-2,2'-diol (BINOL) with H_2O_2 as an oxidant appeared as difficult for researchers. The oxidative coupling of naphthene skeletons has been a powerful technique for producing biaryl derivatives throughout the past few decades due to their wide-ranging advantages in biological activities, organic transformation reactions, materials sciences, catalysts, chiral ligands, etc. Several researchers demonstrated synthetic routes of biaryl derivatives in the presence of molecular O_2 as the oxidant by utilizing chiral and non-chiral metal catalysts. However, the catalytic conversion of 2-naphthol to a biaryl product has various disadvantages when O_2 is present as an oxidant, including a low product yield and a longer reaction period. Since 30% H_2O_2 is regarded as a "green" oxidizing agent with its accelerating capacity for high product yield within a short period, the studies have shifted towards it as the oxidant for the same in recent times. Unfortunately, there is very little chance for the naphthol nucleus to form the biaryl moiety by using H_2O_2 as an oxidant (Scheme 22B). The formation 1,2-naphthoquinone and 1,2-dihydroxynaphthalene as by-products restricted the selectivity and yield of the products. Several reports were successful using H_2O_2 without resulting in any byproducts have several drawbacks such as reaction conditions, product yields, less substrate scope, and use of several additives. Therefore to mitigate such limitations associated with the oxidative coupling reactions our group designed several support-based metal-suitable catalyst systems to transfer 2-naphthol selectively to BINOL without producing any minor products. Our group investigated a good number of catalysts using different zeolite-encapsulated and supported metal catalysts. Several studies on Co_3O_4 and V_2O_5 or their mixed valent oxides have been conducted with varied applications, although the use of Co_3O_4-V_2O_5 oxides in photochemical organic transformation reactions is quite limited. Chiral modification of such mixed metal oxides is not known in the literature. The concept of chiral nanocatalysis is growing in popularity these days, there is large scope in expanding the application of chiral nanoparticle catalysts in asymmetric oxidation. Thereby intrigued by such designs herein it is good for the synthesis of chirally modified Co-V oxide nanocatalyst anchoring on reduced graphene oxide and understand their behavior in asymmetric photo-oxidation of 2-naphthol. Thereby intrigued by such designs herein it is good for the synthesis of chirally modified Co-V oxide nanocatalyst anchoring on reduced graphene oxide and understand their behavior in asymmetric photo-oxidation of 2-naphthol. The chiral modifiers interacted with the Co_3O_4-V2O5/rGO catalyst through different non-covalent interactions and provided a chiral environment to produce enantiomeric excess of C2-symmetric R and S BINOL. After asymmetric synthesis we designed a Ru-nanos supported on zeolite-Y for the selective production of biaryl derivatives from various naphthols molecules.

The biaryls are important organic molecules in numerous fields due to their distinct functional and structural properties used as building blocks in pharmaceuticals, agrochemicals, contributing to developing drugs, pesticides, and biologically active compounds. The biaryls can be achieved by various C-C bond formation reactions between two organic aromatic moieties such as SMCC reaction, Ullmann Coupling, Negishi Coupling, Heck Reaction, Stille Coupling reaction, etc. Each

of these methods has its advantages and disadvantages, with the SMCC reaction being the most popular one due to its broad substrate scope and user-friendly conditions. It was evident from the literature that the SMCC reaction is mostly recognized for the activation of iodo (I) or bromo (Br) aryl halide substrate molecules. But out of those different forms of SMCC reactions, the formation of biaryl products through the activation of the C—Cl bond is significant due to the low cost of the chloro (Cl)-derivatives of aryl halide substrates. Therefore, researchers are trying to replace these Br or I-substrates with the Cl-substrates. For that, Pd-based catalysts, whether in both homogeneous or heterogeneous forms, are widely recognized. Heterogeneous catalysts that are reported for SMCC reaction fails to achieve high success in activating the C-Cl bond. However, we synthesized two heterogeneous catalysts *viz* palladium-iron oxide and palladium vanadiumoxide supported on zeolite-Y (Pd/PdO-Fe_2O_3-Y and Pd/PdO-VO_x-Y_{Cys} respectively) for the C-C bond formation reaction by activating the C-Cl bond of aryl chlorides.

Copper (Cu) based catalysts as well as Mg-SiO_2 are well known for the partial oxidation or dehydrogenation of C_2H_5OH. Herein we have developed copper oxide (CuO) nanocatalyst supported on Mg^{2+}-exchanged zeolite-Y (CuO-Mg-Y) for the *in situ* generation of acetaldehyde (CH_3CHO) from ethanol (C_2H_5OH) and its condensation with different benzaldehydes (BAs) for the selective formation of α, β-unsaturated carbonyl compounds through cross-aldol condensation. We have developed a low-cost, environmentally friendly, and recyclable zeolite-Y supported Fe-oxide catalyst for the peroxymonosulfate-assisted synthesis of 2,2-di(3-indolyl)-3-indolones and isatins from various substituted and non-substituted indoles by simply changing the solvent system and reagent addition method.

Naphthols and such phenolic derivatives are significant compounds due to their applications as biologically active molecules as well as in pharmaceuticals and agrochemicals. These type of important compounds can be synthsied via Fiedel-Crafts alkylation process. The conventional methodologies required various hasre reaction conditions and use of external base. We have synthesized low cost Fe_2O_3-KY for direct C(1)-H functionalization of 2-naphthols with primary alcohols to afforded the substituted naphthalene derivatives using base free method. For the benzylation of phenol we developed Ru-nanocatalysts on zeolite-Y.

2 Methodology

2.1 Synthesis of zeolite-NaY supported Pd/PdO—Fe_2O_3-Y

Synthesis of Fe_2O_3-Y: The iron oxide supported on zeolite-NaY (Fe_2O_3-Y) was synthesized by taking 2 g of zeolite-NaY in 50 mL of 0.2 M $Fe(NO_3)_3 \cdot 9H_2O$ solution was vigorously stirred at 60 °C for 48 h with maintaining a pH of 10—11 (using 1 M KOH solution). The suspension was cooled to room temperature, and allowed to settle for filtration. The material was collected after filtration was washed several times with water. The brownish solid material was then dried in an oven and ground subsequently for few hours. Then it was subjected to calcination process at 500 °C and again ground for 3 h to obtain Fe_2O_3-Y material.

Synthesis of Pd/PdO—Fe_2O_3-Y: To Synthesis of Pd/PdO—Fe_2O_3-Y, 1 g sample of Fe_2O_3-Y was impregnated with 0.01 M $Pd(NO_3)_2$ solution in distilled water, and then it was autoclaved at 100 °C for 60 min. Then it was filtered and washed with distilled water. The obtained material was then dried in a vacuum oven to obtain the desired Pd/PdO—Fe_2O_3-Y catalyst. The synthesized material was characterized by various spectrochemical and analytical tools.

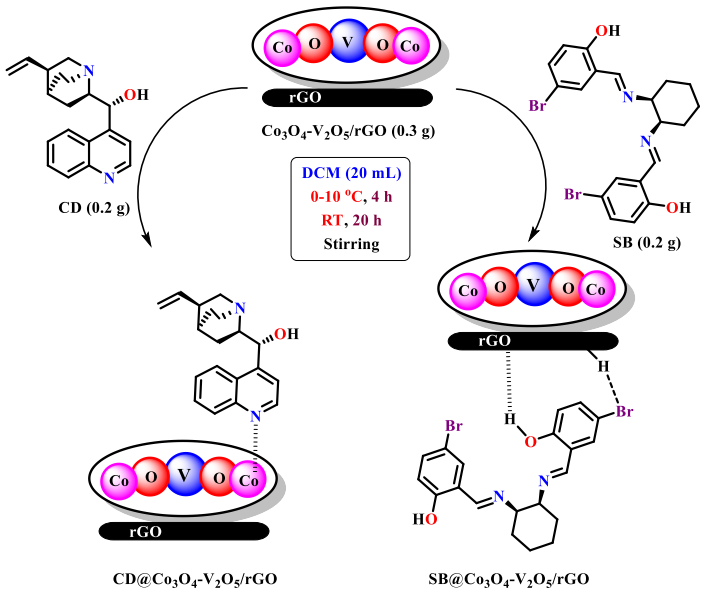
2.2 Synthesis of zeolite-NaY supported Pd/PdO-VO_x-Y_{aa}

Preparation of vanadium oxides (VOx) on zeolite-Y: Vanadium oxides designated as VOx-Y were synthesized by following the post synthesis approach. For this 8 g of zeolite-Y was preheated in an oven at 70 °C for 4 h. 100 mL of a 0.5 M aqueous VCl_3 solution was added to the preheated zeolite-Y and vigorously stirred at 70 °C for 20 h. The mixture was then cooled to room temperature, filtered and washed several times using distilled water to obtain the vanadium exchanged zeolite-Y (V-exchanged-Y) powder. The material was then divided into 4 equal parts (2 g each) for the subsequent treatment with amino acids. During amino acid treatment, 50 mg of each amino acids *viz.* cysteine, proline, serine, and threonine were individually added to 2 g of the synthesized V-exchanged-Y in mortar pestles. The mixtures were then afterward ground for 8 h using small amount of distilled water and EtOH. The grinding process was accompanied by intermittent heating at 90 °C. The VO_x-Y_{aa} (aa=amino acid) materials so obtained were vacuum dried at 100 °C and kept for 20 h in a desiccator.

Preparation of Pd doped vanadium oxides (VO_x) modified with amino acids over zeolite-Y: The synthesis of the bimetallic amino acid modified Pd/PdO-VO_x-Y_{aa} catalyst involved combining a 10 mL 0.5 M aqueous solution of $PdCl_2$ with the prepared amino acid modified zeolite-Y supported vanadium oxides (VO_x-Y_{aa}). The mixture was ground in a similar manner as mentioned in the previous section. This grinding process was performed until the initial light gray solid transformed into greenish to faded greenish solid materials. The final materials were obtained after filtering, followed by washing with distilled water, and dried under vacuum conditions.

2.3 Synthesis of Chirally modified Co_3O_4-V_2O_5/rGO with cinchonidine (CD), Schiff base (SB) ligand.

We have also synthesized Chiral modification with cinchonidine (CD) and performed by the following steps. To 0.3 g of Co_3O_4-V_2O_5/rGO nanocatalyst, a solution of cinchonidine (0.2 g) in dichloromethane (20 mL) was added with continuous stirring under 0-10 °C or 4 h. Then the resulting reaction mixture was stirred for an additional 20 h at room temperature (RT). The reaction mixture was allowed to stand for slow evaporation of the solvent. The obtained residue was collected and dried at RT. Another chiral modification with Schiff base (SB) ligand was done by our own synthesized Schiff base ligand using the similar approach as mentioned in CD modification process. And finally formed SB@Co_3O_4-V_2O_5/rGO (Scheme 1).

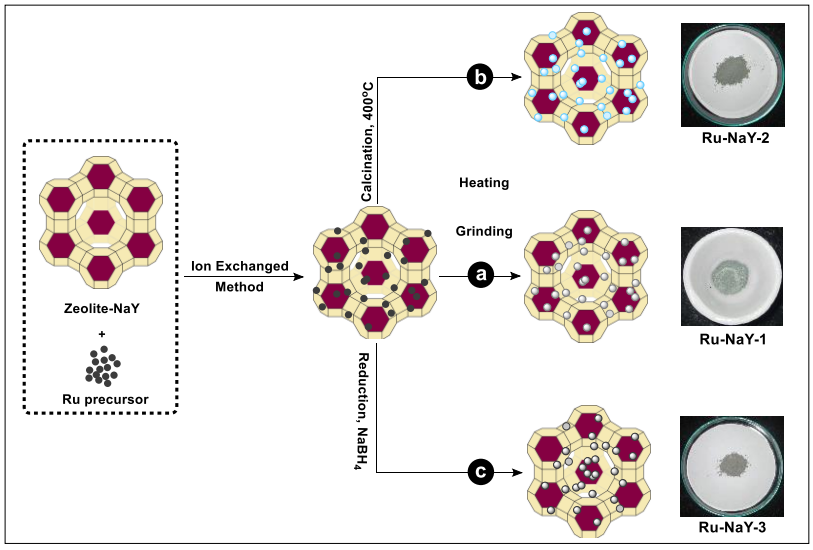


Scheme 1 Schematic representation of chiral modification of Co_3O_4-V_2O_5/rGO with CD and SB ligand.

2.4 Synthesis of zeolite-Y supported ruthenium catalyst

Three different Ru-based catalyst supported on zeolite-Y matrix was synthesized with slight modification in the preparation method. The three catalyst are designated here in as Ru-NaY-1, Ru-NaY-2 and Ru-NaY-3 (Scheme 2). The Ru-NaY-1 was prepared by treating ~ 83 mg of ruthenium chloride (0.01 M solution) in 40 ml of water along with 1g of sodium form of zeolite-Y in 100 mL round bottom flask (RB) with weight ratio of ~ 11.9. The suspension was stirred for 48 h and kept under refluxing condition at 60 °C. The dark-gray solid material was collected by filtering using filter paper (Whatman 41). The material was dried at 120 °C for 16 hours. Finally, the light gray material (Ru-NaY-1) was vacuum dried prior to its characterization. The Ru-NaY-2 was synthesized by subjecting a half portion of Ru-NaY-1 (~ 0.5g) for calcination at 400 °C for 6 h. On calcination the materials change the color from light gray to grayish-blue color.

Ru-NaY-3 was prepared following previously reported ion-exchange method followed by reduction of the metal ions with reducing agent, sodium borohydride ($NaBH_4$). For this, 1 g of sodium zeolite-Y was taken in 100 mL water and mixed well for few minutes in a 250 mL RB. To this zeolite-Y suspension 0.01 M metal salt solution (~ 83 mg ruthenium chloride, in 40 mL H_2O) was added and stirred for 24 hours in a magnetic stir bar at room temperature. The dark blackish-gray color suspension solution turned light gray after drop-wise addition of 50 mL $NaBH_4$ (~300 mg in water) with constant stirring (500-600 rpm) at room temperature. The reducing agent/metal ions ratio were kept over ~ 400-500 times to achieve complete reduction of the metal ions. The resultant grayish material was dried and transferred into closely tight Schleck tube. Finally, the tube was then dried at 70 ºC under vacuum and sample was stored in the Schleck tube under inert condition at room temperature and represented as Ru-NaY-3.



Scheme 2 Schematic representation for synthesis of a) Ru-NaY-1, b) Ru-NaY-2 and c) Ru-Na-Y-3 catalyst.

2.5 Synthesis of copper oxide (CuO) nanocatalyst supported on Mg^{2+}-exchanged zeolite-Y (CuO-Mg-Y).

First, we have synthesized magnesium(Mg^{2+}) exchanged Zeolite-Y(Mg^{2+}-Y). Initially 2 g of Sodium-Y (Na-Y) zeolite was suspended in an aqueous solution containing 0.01 M (0.0507 g in 25 mL water) of $MgCl_2.6H_2O$. This solution was stirred at 60 °C under refluxing conditions for 24 hours and filtered the solution to get Mg^{2+}-Y. Then the CuO was deposited on the surface of zeolite-Y by precipitating copper hydroxide, $Cu(OH)_2$ and its calcination at 400 °C for 6 hours. For this 0.01 M

(0.0426 g) of $CuCl_2 \cdot 2H_2O$ and 0.1 M of sodium hydroxide (NaOH) was used. The colour of the resulting materials was gray and it was collected for catalytic application.

2.6 Synthesis of Zeolite-Y Supported Iron (III) Oxide Nanocatalyst, Fe_2O_3-Y

At the beginning of our project, we have successfully synthesized cost-effective zeolite-Y supported Fe(III) oxide nanocatalyst. In a 100 mL round bottom (RB) flask, 2 g of zeolite-Y was suspended in 50 mL of 0.01 M aqueous solution of $Fe(NO_3)_3.9H_2O$ (0.202 g) maintaining a weight ratio of ~10:1. Subsequently, the solution was made basic (pH ~8-9) by the addition of 1 M KOH solution under continuous stirring at room temperature (RT) to precipitate iron salt as iron hydroxide on the zeolite-Y surface. The resulting solution was filtered using Whatman No. 1 filter paper and the residue was washed with hot water several times. Then the resultant material was subjected to Soxhlet extraction to remove any impurities. The obtained material was dried in an oven at 327 ºC (600 K) for 12 h and finally dried under vacuum condition for 3 h. The final light brown color Fe_2O_3 nanoparticles supported on zeolite-Y i.e., Fe_2O_3-Y was collected for catalytic use.

2.7 Synthesis of iron oxide supported on potassium exchanged zeolite-Y (Fe_2O_3-KY)

We have also synthesized iron oxide supported on potassium exchanged zeolite-Y (Fe_2O_3-KY). For this 2 g of zeolite-HY was mixed with aqueous solution in a round bottom flask and then 50 mL of 0.1 M potassium chloride (KCl) was added to the suspension and stirred for 48 hours under refluxing condition at 60 °C. To this exchanged zeolite-Y (K-Y), 50 mL of 0.1 M of sodium hydroxide (NaOH) solution and 0.01 M (0.135 g in 50 mL water) of iron (III) chloride solution were added dropwise. The mixture was then stirred under refluxing condition for 24 hours.The light yellowish solid material was obtained by simple filtration method and washed with warm water. The solid materials was washed several times with water until it gave negative silver nitrate ($AgNO_3$) test. Then it was subjected to calcination at 400 °C for 5 hours to get the desired Fe_2O_3-KY materials. The material was vacuum dried prior to its characterization and application. The synthesized materials are characterised via analytical/spectroscopical technique like XRD, TEM, SEM, EDX, XPS, TPD, NMR etc.

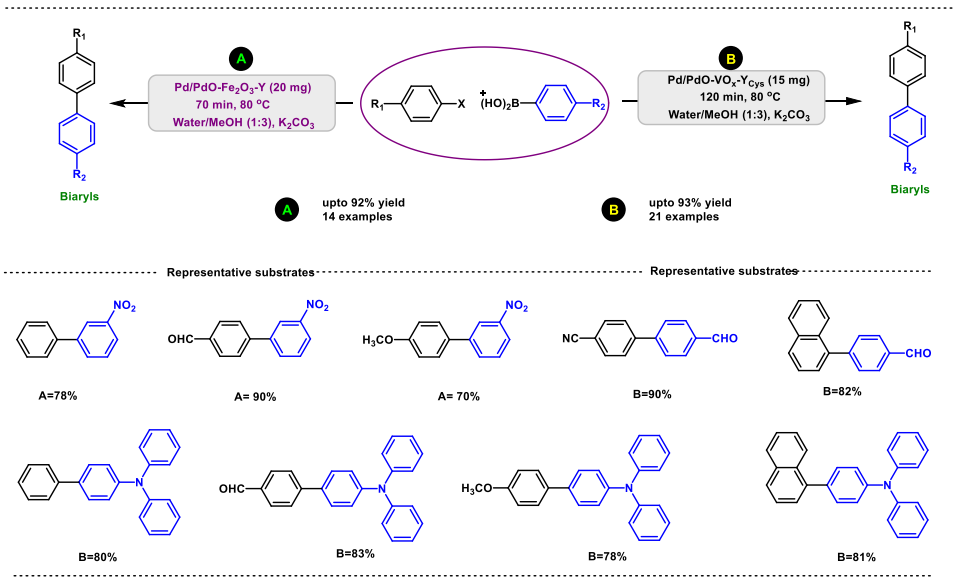
3. Results and Discussion: Salient Research Achievement

3.1 To study the catalytic ability of the synthesized catalysts in various C-C bond formation reactions

After synthesis of various metal catalysts then we employed them for various targeted C-C bond formation reactions. They are described briefly in the followings sections.

3.1.1 Suzuki Miyaura Cross-Coupling (SMCC) reaction

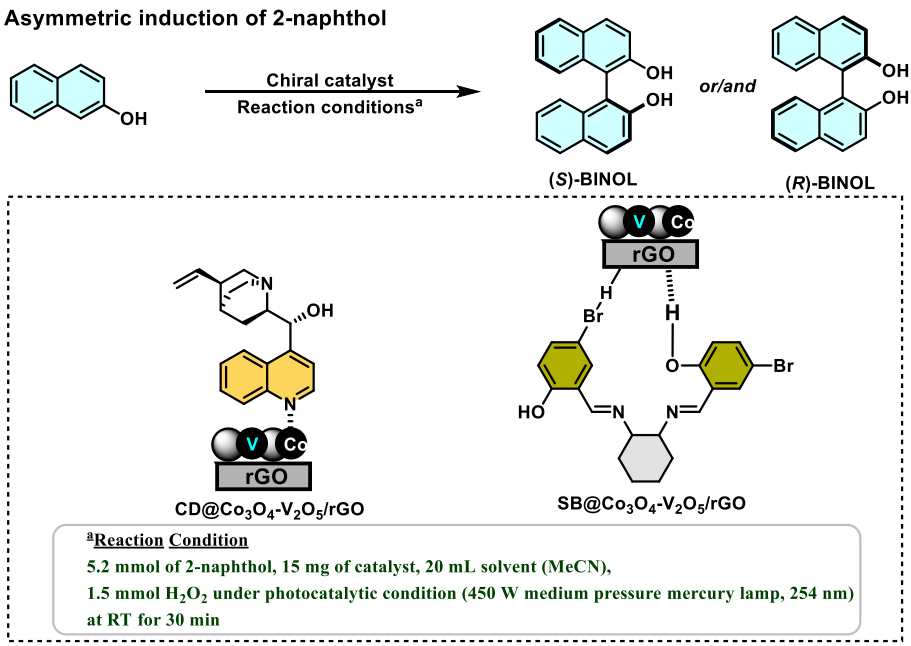
In literature, although a good number of catalytic systems have already been reported, studies that can influence the properties of Pd with a low-cost metal like iron (Fe), especially with zeolite-NaY support, have not been explored. Therefore, we have synthesied dual metal matrix in zeolite-NaY i.e., Pd/PdO—Fe_2O_3-Y, with low Pd content heterogeneous, with high selectivity and high TON has been designed to overcome the boundaries associated with chloro (—Cl) substituted aryl halides in the SMCC reaction (**Scheme 3**). The optimal reaction conditions were different than the previous reports with 15 mg of Pd/PdO-VO_x-Y_{Cys}, a 3:1 CH_3OH/H_2O solvent system, 3 equivalents of K_2CO_3 as a base, at 80 °C for 2 hours affording a 93% yield of the corresponding biaryl product. The catalyst demonstrated broad applicability or substrate scopes, coupling various aryl chlorides with arylboronic acids to afford high yields. The reaction provided good yield with both electron-donating and electron-withdrawing substituents.



Scheme 3. Shematic reprentation of SMCC for synthesis of biaryls derivatives in presence of (A) Pd/PdO−Fe_2O_3-Y and (B) Pd/PdO-VO_x-Y_{aa}.

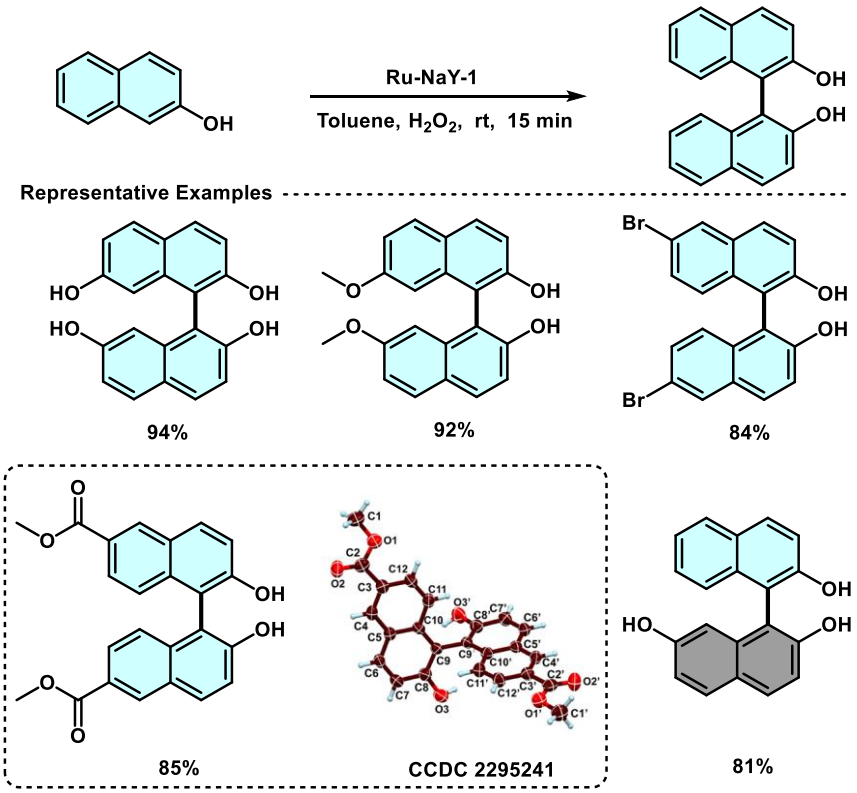
3.1.2 Oxidation of 2-naphthol and its derivatives to BINOLs

Our initial work with the oxidative coupling of 2-naphthol started with the very first time introduced a chirally modified Cr-V metal catalyst decorated on reduced graphene oxide (rGO) for asymmetric enantioselective photo-oxidation reaction. The nanocatalyst was chirally modified with cinchonidine and Schiff base ligands (Scheme 4). The asymmetric induction was found to be different concerning chiral modification. The *S*-(*ee* 83%) and *R*-isomer (*ee* 92%) were produced predominantly while metal oxide was modified with cinchonidine and Schiff base ligands respectively.



Scheme 4. Oxidative coupling of 2-naphthol to BINOL in the presence of synthesized cobalt-vanadium oxide catalysts under optimized conditions

The Ru-based nanocatalyst that was utilized for benzylation of phenol showed high activity for the selective synthesis of biaryl derivatives. The catalyst provided yield up to 94% of various biaryl derivatives in toluene within a very short period, i.e., 15 minutes with H_2O_2 as oxidant (Scheme 5).

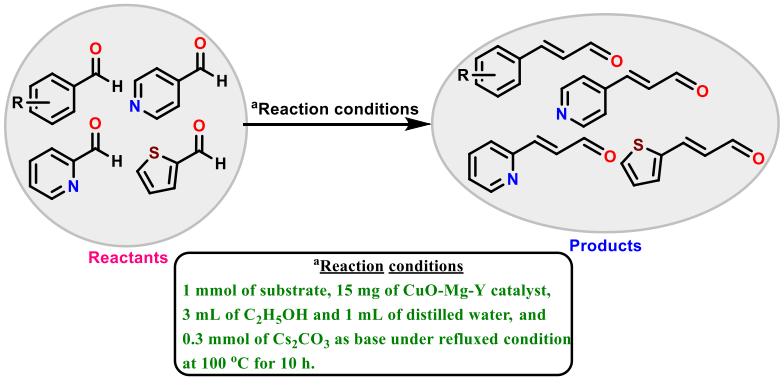


Scheme 5. Oxidative coupling of 2-naphthol to BINOL in presence of synthesized Ru-NaY-1 catalyst under optimized conditions.

Hence our present work with experimental and theoretical evidence can help the researchers to design and rationalize new heterogeneous catalysts for the oxidative C-C coupling of 2-naphthols. The superior activity of of Ru-NaY-1 compared to Ru-NaY-2 and Ru-NaY-3 was attributed to various factors i) the presence of more Lewis acid and Brønsted acid sites, ii) presence of high valent Ru-species and iii) the Ru loading. Ru-NaY-1 possessing both Ru(III)/Ru(IV) species favoured and boosted the oxidative coupling of 2-naphthols. The presence of low valent Ru-center in other two catalysts as observed from XPS analysis probably hampered the catalytic activity by lowering the Lewis acidity and alternating the redox potential.

3.1.3 Synthesis of α, β-unsaturated carbonyl compounds via cross aldol condensation process

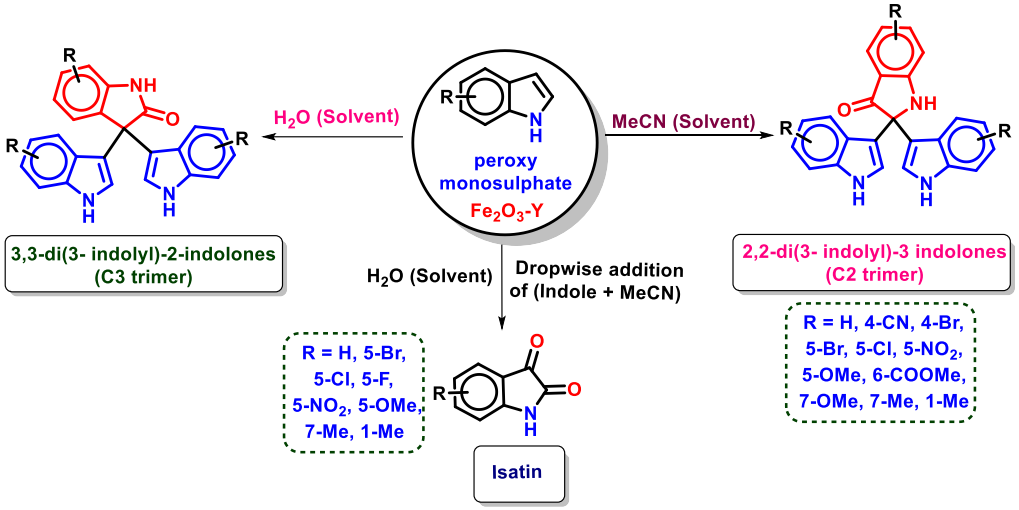
Copper (Cu) based catalysts as well as Mg-SiO_2 are well known for the partial oxidation or dehydrogenation of C_2H_5OH. Intrigued by the ability of Cu and Mg-based catalyst for the synthesis of CH_3CHO from C_2H_5OH herein we tried to develop copper oxide (CuO) nanocatalyst supported on Mg^{2+}-exchanged zeolite-Y (CuO-Mg-Y) for the *in situ* generation of CH_3CHO from C_2H_5OH and its condensation with different benzaldehydes (BAs) for the selective formation of CA through cross-aldol condensation (Scheme 6).



Scheme 6. Synthesis of different α, β-unsaturated aldehydes or cinnamaldehyde derivatives in presence of CuO-Mg-Y catalyst.

3.1.4 Synthesis of C2, C3 trimers, and isatins from indoles

A cost-effective and reusable Fe-oxide catalyst supported on zeolite-Y was developed to selectively synthesize C2 di-indolyl indolones and isatins (Scheme 7). The activity of the Fe_2O_3-Y was found to be more advantageous in comparison to the other reported noble metal-based catalysts. The activity of the Fe_2O_3-Y was found to be more beneficial in comparison to the other reported noble metal-based catalysts. Most of the C2 trimerized products were isolable through the force precipitation technique without involving any chromatographic separation method. This will further reduce the cost of the product isolation technique and also limit the use of solvents that are usually employed for chromatographic separation. Further, the catalyst was also recyclable upto five consecutive cycles without hampering the % yield of the desired product.



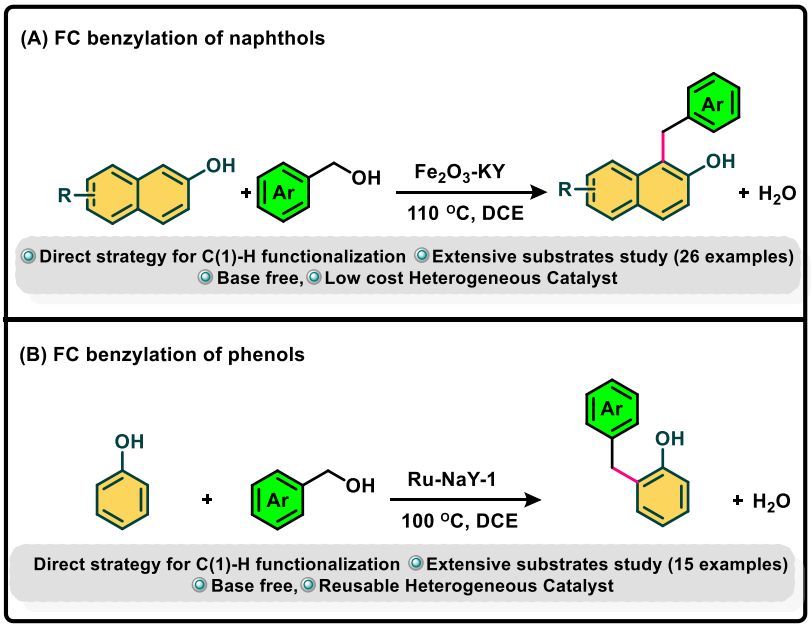
Scheme 7. Synthesis of C2, C3 trimers, and isatins in presence of Fe_2O_3-Y nanocatalyst.

3.1.5 Friedel-Crafts benzylation reaction

Naphthols and such phenolic derivatives are significant compounds due to their applications as biologically active molecules as well as in pharmaceuticals and agrochemicals. These type of important compounds can be synthsied via Fiedel-Crafts alkylation process. The conventional methodologies required various hasre reaction conditions and use of external base. We have synthesized low cost Fe_2O_3-KY for direct C(1)-H functionalization of 2-naphthols with primary

alcohols to afforded the substituted naphthalene derivatives using base free method (**Scheme 8A**). The exchanged alkali metal cations played an important role through cation-π interaction in bringing the product selectivity and governing the product yield.

The utilization of ruthenium (Ru) based catalyst supported on zeolite-NaY matrix, a true heterogeneous catalyst system addressed the limitations associated with the superior *ortho*-benzylation of phenol (**Scheme 8B**). Various benzylated phenol derivatives were obtained with high yield (up to 89%), high selectivity with this catalyst system. A detailed investigation of three different types of Ru-catalysts provided the information that creation of strong Lewis acid sites with high valent Ru-species endorsed high productivity along with high *ortho*-selectivity in benzylation of phenols. The theoretical calculations (DFT) have provided good evidence for the reaction mechanism and stability of the intermediate.



Scheme 8. FC benzylation of (A) naphthols derivatives in presence of Fe_2O_3-KY and (B) phenol derivatives catalyzed by Ru-NaY-1.

4 Salient Research Achievement: Application Potential

- Pd with a low-cost metal like iron (Fe), especially with zeolite-NaY support, have not been well established. Herein we have synthesized very low Pd loading (0.0037 mol %), a true heterogeneous catalyst for activation of the robust C—Cl bond of aryl chlorides in the Suzuki—Miyaura cross-coupling (SMCC) with various derivatives of aryl chlorides (Ar—Cl). Various biaryl derivatives were obtained with high yield (up to 92%), high selectivity, and good TON (249) with this Pd/PdO—Fe_2O_3-Y catalyst. The charge transfer from Fe to Pd and the modification of basic sites in the catalyst in the presence of zeolite-NaY played a crucial roles in the C—Cl bond activation process. The theoretical calculations (DFT) have provided good evidence that the presence of Fe changes not only the electronic structure of Pd but also its reactivity in terms of chemical potential and hardness. Hence our the present work with experimental and theoretical evidence can help the researchers to design and rationalize new heterogeneous catalysts for the C—Cl bond activation process. The use of peculiar Fe with the ability of variable oxidation states (II to VI) to have a charge transfer transition that make electron enriched Pd enhances the oxidative addition step in this C-Cl bond activation reaction.

- To synthesized chiral modified heterogenous catalyst for chiral synthesis of product, we developed Chirally modified cobalt-vanadate grafted on battery waste derived layered reduced graphene oxide for enantioselective photooxidation of 2-naphthol. The synthesized materials are characterised via analytical/ spectroscopical technique like XRD, TEM, SEM, EDX, XPS, TPD, NMR etc.
- The CuO nanoparticle supported on Mg^{2+}-exchanged zeolite-Y served as a low-cost metal catalyst for selective dehydrogenation of ethanol to acetaldehyde. The main advantages of the present catalyst with the previous one are the catalyst is cheaper, less toxic and provides a scope for wide range of substrates.
- The synthesized indole C-2 trimerized product and other produced cinnamaldehyde products contain potential for pharmaceutical activity. The synthesized chiral BINOL product are regarded as important chiral auxiliaries
- A cost-effective and reusable iron oxide supported on potassium exchanged zeolite-Y (Fe_2O_3-KY) was developed for the direct C(1)-H functionalization of 2-naphthols with primary aromatic alcohols. The studied revealed that exchanged alkali metal cations played an important role through cation-π interaction in bringing the product selectivity and governing the product yield.
- The superior activity of of Ru-NaY-1 compared to Ru-NaY-2 and Ru-NaY-3 was attributed to various factors i) the presence of more Lewis acid and Brønsted acid sites, ii) presence of high valent Ru-species and iii) the Ru loading. Ru-NaY-1 possessing both Ru(III)/Ru(IV) species favoured the FC benzylation process and at the same time it boosted the oxidative coupling of 2-naphthols. The synthesized materials have lot more potential towards organic synthesis like cross-coupling reaction, C-C coupling reactions etc. The synthesized indole derivatives, biaryl products and other naphthalene derivatives contain high potential for biological and pharmaceutical activity.
- Several research articles related to C-C bond formation reactions have been published in various reputed journals by fully acknowledging this scheme [**Ref 1-7**]. Besides C-C bond formation reactions this scheme also provides us the opportunity to explore the methanol oxidation reactions, to design beneficial routes for addressing several environmental issues, etc [**Ref 8-23**].

5 Conclusion and Future Scope

The project scheme summarizes various C-C bond formation reactions using different nanocatalysts supported on zeolite-Y. It has brought out some of the certain advantages of zeolite-supported nanocatalysts, particularly on C-Cl bond activation processes in SMCC reaction, oxidative coupling of naphthols, 3,3'-bis(indolyl)methanes synthesis, C2 trimerization of indole, FC benzylation reactions. More significantly the utilization of ethanol as sources of acetaldehyde in the synthesis of β-aryl enals derivatives is expected to provide a new dimension in developing greener protocols. It also provides the utilization of low-cost Fe_2O_3-Y for the C2-trimerization of indoles. At the same time, the screening of various nanocatalysts in the oxidative coupling of naphthols will help the research community look for a suitable catalyst for the synthesis of naphthols derivatives under a peroxide environment. We believe that the information provided through this scheme will certainly help the researchers gain knowledge, especially in the utility of zeolite-supported nanocatalysts in C-C bond formation reactions. As our research is an interdisciplinary one. Hence, multiple beneficiaries within the commercial private sector, policy-makers (nationally and internationally), and local government agencies and regulators are all likely to benefit from the research outcome. As the research project will generate new knowledge (methodologies, tools, and techniques for researching), the project outputs will result in an improved understanding of the new drug design methodology for pneumonia treatment via C-H bond activation of phenolic compounds. Thus, improved effectiveness of the health sector and, welfare, a better environment with sustainability are inevitable outcomes of this work

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FORM-L
UTILISATION CERTIFICATE

COUNCIL OF SCIENTIFIC AND INDUSTRIAL RESEARCH

Human Resource Development Group
CSIR Complex, Library Avenue, Pusa, New Delhi – 110012

CSIR-HRDG Scheme No. : 80(0094)/20/EMR-II

S.No.	Particulars	Letter No. /Bank Transaction ID Nos. & Date	Amount
1	Grants received from CSIR during the **year (01.04.2023 to 31.03.2024)**	F No. **80/0094/20/EMR-II** Dated: **16.06.2025** **(TSA-Hybrid)**	**6,94,000**
2	Unspent balance of previous year		**23**
3	Interest earned/accrued on CSIR grant	**NIL**	**NIL**
Total			**6,94,023**

1. Certified that out of Rs. **6,94,000.00** (Rupees **six lakh ninety-four thousand only**) of grant-in-aid released by Extramural Research (EMR) Division of HRDG (CSIR) vide letter No./Bank Transaction ID Nos. **F No. 80/0094/20/EMR-II** dated **16.06.2025** as given above during the year **01.04.2023– 31-03-2024** and Rs **0.00** earned/accrued as interest from bank on grants released by CSIR and Rs. **23.00** on account of unspent balance of the previous year, a sum of Rs. **6,94,023.00** has been utilized for the purpose for which it was sanctioned and that the balance of Rs. **0.00** remaining unutilized at the end of the year and will be adjusted towards the grant-in-aid payable during the next year.

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

it was sanctioned. The detail expenditure incurred during the year is shown in the enclosed "Statement of Accounts (Receipt & Payment)".

(Kinds of checks exercised)

1. Vouchers and Statement of Accounts
2. Grant-in-Aid
3. Expenditure Register
4. Bank statements for accrual interest
5.
6.

Signature of Authorised Officer
with Date & Seal
Finance Officer
Tezpur University

Countersigned by Registrar/Dean/ Director
of the institute with Date & Seal
Registrar
Tezpur University

The Utilization certificate and statement should be signed by Head of the Finance & Accounts and countersigned by Registrar/Dean/Director of the University/Institute.

ANNEXURE – II

Consolidated Statement of Accounts

(For the Financial Year 01.04.2023 – 31.03.2024)

Scheme Number : **80(0094)/20/EMR-II**

Title of the Research Scheme : **Design of Zeolite-Y Supported Heterogeneous Catalyst for C-C Coupling Reactions**

Name of the Principal Investigator : **Dr Kusum K Bania**

Date of Commencement : **01.10.2020** Date of Termination : **30.09.2024** ↓

Receipts (Particulars of grants received)							Payments (Particulars of grants spent)					
Period (ending 31 March)	Transaction No., date & Amount	Stipend (Rs.)	Contin-gency (Rs.)	Equipment Grant (Rs.)	HRA / MA or Over-head	**Total (Rs.)**	Stipend (Rs.)	Contin-gency (Rs.)	Equipment Expenses (Rs.)	HRA / Med Allowance or Overhead Charges	**Total (Rs.)**	**Balance (Rs.)**
01.04.2023 to 31.03.2024	**F No. 80/0094/20 /EMR-II, 16.06.2025 & 6,94,000**	4,44,000	250,000	NIL	NIL	**6,94,000**	4,44,000	250,000	NIL	NIL	**6,94,023**	**0**
	Amount from previous year	0	23	NIL	NIL	**23**	0	23	NIL	NIL	**0**	**0**
TOTAL		**4,44,000**	**250,023**			**6,94,023**	**4,44,000**	**250,023**			**6,94,023**	**0**

Signature of Registrar With Stamp

Registrar
Tezpur University

Name: Prof. Chandan Goswami
(Registrar (i/c), Tezpur University)

Signature of Finance Officer With Stamp

Finance Officer
Tezpur University

Name: Prof. Robin Doley
(Finance Officer (i/c), Tezpur University)

Signature of Principal Investigator With Stamp

Name: Prof. Kusum K Bania
(Principal Investigator)