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Topotactic transformation of homogeneous phosphotungastomolybdic acid to heterogeneous solid acid catalyst for carbohydrate conversion to alkyl levulinate

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Highlights

- Design and synthesis of the noble 3D polymetallic acidic catalyst.
- Acidity Control synthesis materials by use of capping agent.
- Use of as-synthesis materials for selective dehydration and etherification of carbohydrate to ethyl levulinate

1. Introduction

The directed and intense interaction of higher transition metal oxide with inorganic non-metals can be promising for generating high acidic three-dimensional materials by design. A comprehensive controlled the acidity of heteropoly acid-like molecules and interpretation of the microstructure and mechanism of the formation of a versatile heterogeneous solid acid catalyst HPWMoOx has been attempted to heterogenized. Biomass-Derived cystine as organic linkers to control the acidity as-synthesized materials, which have greater acidity and complexity in separation from the reaction mixture. The new and unique results obtained in catalysis done in biphasic reaction. Cystine binds with the surface of HPWMoOx, and the topotactic transition occurred, change the morphology and lattice parameter. We described here a sustainable transformation of highly acidic heteropoly acid (HPWMoOx) to cystine anchored on the active surface of the heteropoly acid and controlled the acidity and heterogenized the materials. As-synthesized materials have been showing high catalytic activity for the direct formation of alkyl levulinate and furanics intermediate from carbohydrates. The analytical analysis of as-synthesis materials done by NH3-TPD, BET, XRD, FESEM, TEM, HRTEM, FTIR, ATR, TGA, DTA to stabilized the morphology and acidity controlled mechanism.

2. Methods

Two types of poly acidic materials prepared (i), HPW4Mo10Ox and (ii) $HPW_4Mo_{10}Ox$–Cys $H_5PW_2Mo_{10}O_{40}$ was prepared in a two-step. In first step 1 equivalent dehydrated K_2HPO_4 (before used, vacuum dry at 120 °C for 4 h) dissolved in 50 mL hot water, labeled solution (A). In 2nd 100 mL beaker, 4 equivalent of $Na_2WO_4.2H_2O$ dissolved in 50 mL hot water and labeled solution (B). Solution (B), drop added in solution (A) and stirred for 5 min at the hot condition, then cool the reaction mixture in an ice bath, then 2.5 mL concentrated H2SO4 added as precipitating agent. After addition of H2SO4, white precipitate form. In second step 10 equivalent of $Na_2MoO_42H_2O$ dissolved in 60 mL distil water, stirred at room temperature 5 min, then added drop-wise in the first step solution, after addition of ~5 mL, white colour diapered, then continuous addition, colourless solution obtained, the final solution composition is 1:4:10 (K_2HPO_4 : $Na_2WO_4.2H_2O$: $Na_2MoO_{42}H_2O$). In colorless solution, one drop chilled H_2SO_4 added green precipitate formed, after shaking green precipitate dissolved, then continuous dropwise added till the green-yellowish precipitate persist.

3. Results and discussion

To reveal the nature of active sites that favor the formation of selective dehydration-rehydration and etherified products, we resorted to multiple characterization techniques to investigate the functionality and structure of the multifunctional catalyst. Catalysts optimization is achieved through the tone of various parameters, including selectivity of the desired product, the stability of catalyst, and recyclability of the catalyst. Similarly, after using the capping agent cystine, change the number of active acidic sites of as-synthesized materials, which enhanced the selectivity of the desired product. In a microwave irradiation

reaction, the catalyst amount, the temperature is optimized to control the better selectivity of the desired intermediate and thus the enhanced the final product selectivity. Our approach to heterogenized and controlling the acidity of HPA, affords various advantages: (i) the catalyst system can show greater reactivity and selectivity like a homogeneous catalyst. Which is conventional heterogeneous catalysts could not show; (ii) unlike most homogeneous catalysts with comparable performance, the heterogenized HPWMoOx-cys can be recycled;(iii) drastically enhanced the selectivity of the desired product and stopped the rehydration of furanics. Here, we provided future direction for the heterogenization of HPA and used the effective solid acid catalyst.

The topotactic control of two different heteropoly acid materials is one of the components in the catalysis that most used for the selective synthesis of organics. As the heteropoly acid, have high catalytic strength, very tedious to control the selectivity of the desired product, after capping the active acidic sites by cysteine, drastically controlled the acidity and enhanced the desired product selectivity. Cysteine has active amine functional group to be bound to the acidic sites and control the acidity and also heterogenization the materials. The deposition and anchoring of cystine on the active sites of HPMoOx resulted from the ionic interaction between the amine groups of cysteine with a metal center. This interaction prevented the leaching of metal in the reaction mixture even under hot-liquid phase reaction condition under microwave irradiation. The supported material displayed no detectable leaching of metals under hot-plate filtration test and is this regards functioned as true heterogeneous catalysts..

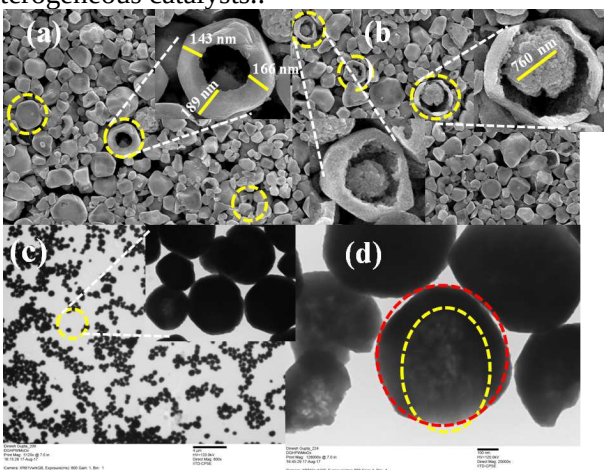

Figure 1. Representative SEM and TEM images of monodispersed hollow core-shell particles of as-synthesized HPW4Mo10Ox

4. Conclusions

Highly stable, 3D hexagonal hollow core-shell structure of HPA has been synthesized. The use of capping agent, changes in the morphology is obtained. Structural characterization and acidity measurement show excellent control of acidity and morphology achieved by using cystine as a capping agent. The dehydration and etherification reactions show different selectivity of the product by using HPW4Mo10Ox and HPW4Mo10Ox-Cys catalyst. The NMR and GC results studies suggest that the HPW4Mo10Ox-Cys materials is only capable for selective dehydration mono-sugars to HMF and HPW4Mo10Ox materials show high degree of Brønsted and Lewis acidity and formed HMF and LA combine..

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[2] B. Zhang.; H .Asakura; J.Zhang.; S. De,.; N. Yan,., Angewandte Chemie International Edition **2***55* (29), (2016)**,** , 8319-8323.
[3] M. G, Mazzotta, D .Gupta,. B Saha,. A. K Patra, A. Bhaumik, M. M. Abu-Omar, ChemSusChem 2014, 7 (8), 2342-2350.

Keywords
" Solid acid, biomass conversion, acidity controlled binder effect, green catalysis,"

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EDUCATION

Ph.D., Inorganic Chemistry (Research advisor: Dr. Basudeb Saha)	Delhi University 2010-2015
M.Sc., Inorganic/Analytical Chemistry (1st Div.)	D.D.U. Gorakhpur University 2010
B.Sc., Chemistry, Microbiology (1st Div.)	D.D.U. Gorakhpur University 2008

PROFESSIONAL APPOINTMENTS

- National Post Doctoral Fellow, Catalytic Reaction Engineering, Department of chemical Engineering, Indian Institute of Technology, Delhi from 09 August 2016 to till date
- Scientist, Research and Development, working on fixed bed reactor, Jubilant Life Sciences 03/2016-to 08/2016
- Institutional Post Doctoral Fellow, Green and Catalytic reaction Lab, Department of Chemistry, Indian Institute of Technology, Kanpur 02/2015 to 02/2016
- Senior Research Fellow, Center for Heterogeneous Catalytic Conversion of Biomass to Biofuels, Department of Chemistry, University of Delhi 2010-2012
- Junior Research Fellow, Center for Heterogeneous Catalytic Conversion of Biomass to Biofuels, Department of Chemistry, University of Delhi 2012-2015
- Project Fellow, Department of Chemistry, D.D.U. Gorakhpur University 2009-10

WORKING EXPERIENCE:

1. Design, synthesis and characterization of different mesoporous, C/Si/Al supported materials and application in catalysis.
2. Design and synthesis of Cu-Zn/Zeolites for CO_2 + H_2 conversion to methanol in continues reactor.
3. Ni-Zn/Al_2O_3 design and synthesis of ethanol reforming in fixed bed reactor.
4. Intermediate hydropyrolysis of biomass (sugar cane bagasse) to biofuels and value added chemicals.
5. Catalytic hydrogenations of 5-hydroxymethylfurfural to 2,5-dimethylfuran and levulinic acid to gamma-valerolactone use as fuels and solvent respectively.
6. Design of shape, size selective CeO_2 as catalyst for p-Xylene Oxidation in water.
7. Biopolymer surface templating inorganic-organic material synthesis and use for biomass valorizations.

8. Use and handling fixed bed and fluidized bed reactor for organic synthesis.
9. Use and handling high-pressure reactor (Parr reactor) for Organic and material synthesis.
10. Use and handling of Microwave for Green-Synthesis.
11. Materials preparation by ball milling methods.
12. Product quantification done by GC, HPLC, ^{1}H-NMR.
13. Materials characterized by: XRD, XPS, EPMA, FESEM, HRTEM, TGA, DTA, FESEM, FTIR, Floriscence, UV-Visible, NMR, GC-Mass, HPTLC, HPCL and etc.,
14. Instruments Handle: GC, HPLC, FTIR, XRD, FTIR, TGA, SEM and NMR

CURRENTLY WORKING ON:

NPDF-Project, titled "Design and synthesis of inorganic-organic hybrid heterogeneous materials and uses in catalysis to investigate solution to some of the environmental concern". (Project No. PDF/2016/000458)

AWARDS AND HONORS:

- National Post Doctoral Fellowship from DST-SERB-2016-2018
- Young Research Scientist Awards from Royal Chemical Society, 2014-15
- Institutional Post Doctoral Fellowship from, IIT Kanpur-2015-16
- CSIR-NET-JRF- All India 073 rank 2011
- GATE-223 Score 2012
- 2nd Position in PhD Entrance Examination, Department of Chemistry, University of Delhi 2010
- One of my ChemSusChem paper most Accessed 05/2014

RESEARCH INTEREST:

Design and synthesis of heterogeneous Zeolites and carbon supported materials, basically solid acid and bifunctional catalyst and application in biomass conversion as hydrolysis, dehydration, isomerization, reduction, chemoselective oxidation of alcohol, aldehyde, methyl arenes, deoxygenation of plate-form chemicals to fuels. Specially focus on reduction of hazard, to achieve increased understanding of molecular basis of sustainability.

TEACHING INTEREST:

Major: Inorganic Chemistry/ Analytical Chemistry/Bio-Inorganic Chemistry
Topic :

- Organometallic and Co-ordination Chemistry
- Spectroscopy and Analytical Techniques
- Inorganic reaction mechanism & catalysis and bio-inorganic Chemistry,
- Group theory and Chemistry of s, p, d & f block elements,
- Chemistry of boron and silicon compounds & ligand field theory
- Organotransition metal Chemistry and advanced bio-inorganic chemistry.
- Metal Complexes, Inorganic materials & nuclear and radiochemistry

PROFESSIONAL AND SCHOLARLYASSOCIATIONS:

- India Catalysis Society, member 2011-present
- Green Chemistry Network Centre member 2010-present
- Royal Chemical Society, member 2011-2012
- American Chemical Society, member 2011-2012

MAJOR RESEARCH ACCOMPLISHMENTS:

- Design and Synthesis of new carbonaceous material for the biomass up-gradation to value added Chemicals and fuels.
- Active surface exposed CeO_2 nanoparticles are used as effective heterogeneous catalyst to oxide para- xylene to terephthalic acid in green condition.
- Porous organic polymer-loaded Fe (III) catalyst efficiently oxidized HMF to the corresponding dicarboxylic acid, FDCA, with O_2 as the oxidant in aqueous medium. This biorenewable dicarboxylic acid is a promising replacement for petroleum-based terephthalic acid for green polyester production.
- **Sugar to fuel:** A large-pore mesoporous tin phosphate material is synthesized hydrothermally by using Pluronic triblock copolymer as the template. This material shows high thermal stability and catalyzes naturally abundant carbohydrates in the aqueous phase to 5-hydroxymethylfurfural, which is a potential bio-based platform chemical to produce a broad range of chemicals and liquid transportation fuels.
- Defined the kinetics and mechanism for selective chemical reduction of biomass fraction to biofuels.
- Design of 3-Dimensionally Self-assembled CeO_2 Nanocube as a Breakthrough Catalyst for Efficient Alkylarene Oxidation in Water.

TEACHING:

Undergraduate: General Chemistry (1 term, Miranda Collage, University of Delhi as Guest Lecturer),
Inorganic Chemistry/Polymer Chemistry (1 term at Institute of Home Economics, University of Delhi).

RESEARCH ARTICLE: (Total Citations 221, h-index=5)

As Corresponding Author:

1. **Dinesh Gupta***, Basudeb Saha, Kamal K. Pant, Titania nanoparticles embedded in functionalized carbon for the aqueous phase oxidation of 5-hydroxymethylfurfural , *Molecular Catalysis 435 (2017) 182–188*, (ISSN: 1381-1169), IF =3.95
2. **Dinesh Gupta***, Anju Mishra, Sabuj Kundu, Cu (II)-β-CD as Water-Loving Catalyst for One-Pot Synthesis of Triazoles and Biofuels Intermediate at Room Temperature without Any Other Additive, *Chemistry Select* 2017, 2, 2997- 3008, (ISSN: 2365-6549), IF= waiting.
3. Samuel Kassayea, **Dinesh Gupta***, Sapna Jain, Kamal. K. Pant, Application of nanocatalyst materials for the sustainable development of green energy, Current Organic Chemistry, 2017, Volume XX, (ISSN: 1875-5348), IF =1.949

As First Author/equal contribution/Co-authors

4. **Dinesh Gupta**, Sabuj Kundu, Basudeb Saha, Efficient Dual Acidic Carbo-Catalyst for One-pot Conversion of Carbohydrates to Levulinic Acid, ***RSC Adv.,* 2016**, **6**, 100417-100426, (ISSN 2046-2069), IF=3.829
5. Kalyanjyoti Deori*, **Dinesh Gupta***, **(***equal contributions) Basudeb Saha, Sasanka Deka, Design of 3-Dimensionally Self Assembled CeO_2 Nanocube as a Breakthrough Catalyst for Efficient Alkylarene Oxidation in Water, ***ACS Catal.* 2014, 4**, 3169−3179, (ISSN 2155-5435), IF =9.307
6. **Dinesh Gupta**, Ejaz Ahmad, Kamal K. Pant, Basudeb Saha, Efficient utilization of potash alum as a green catalyst for production of furfural, 5-hydroxymethylfurfural and levulinic acid from mono-sugars, ***RSC Adv.***, **2017**,**7**, 41973-41979, IF=3.829.
7. **Dinesh Gupta** and Basudeb Saha, Carbon Nanosphere Supported Ru Catalyst for Upgrading of Biomass Intermediates into Natural Herbicide and Chemicals, **Catalysis Communications**, **2017, 100**, 206–209, (ISSN: 1566-7367), IF = 3.389.
8. Basudeb Saha, **Dinesh Gupta**, Mahdi M. Abu-Omar, Arindam Modak, Asim Bhaumik, Porphyrin based porous organic polymer-supported iron (III) catalyst for efficient aerobic oxidation of 5-hydroxymethyl-furfural into 2, 5-furandicarboxylic acid, ***Journal of Catalysis*** , **2013**, **299**, 316–320. (ISSN: 0021-9517), IF=7.354.
9. Kalyanjyoti Deori**, Dinesh Gupta**, Basudeb Saha, Satish K. Awasthi and Sasanka Deka, Introducing nanocrystalline CeO_2 as heterogeneous environmental friendly catalyst for the aerobic oxidation of para-xylene to terephthalic acid in water, ***Journal of Materials Chemistry A***, **2013**,1,7091-7099, (ISSN 2050-7496), IF=8.262.
10. A. Dutta, **D. Gupta**, A. K. Patra, B. Saha and A. Bhaumik, Synthesis of 5-Hydroxymethylfurfural from Carbohydrates using Large-Pore Mesoporous Tin Phosphate, ***ChemSusChem***, ***2014***, 7, 925–933 (ISSN: 1864-564X), IF = 7.116.
11. Michael G. Mazzotta, **Dinesh Gupta**, Dr. Basudeb Saha, Dr. Astam K. Patra,Prof. Dr. Asim Bhaumik, Prof. Dr. Mahdi M. Abu-Omar, Efficient Solid Acid Catalyst Containing Lewis and Brønsted Acid Sites for the Production of Furfurals, ***ChemSusChem*, 2014, 7** (8), 2342–2350, (ISSN: 1864-564X), IF = 7.116.
12. Ashish Bohre, **Dinesh Gupta**, Md. Imteyaz Alam, Rakesh K. Sharma, and Basudeb Saha, Aerobic Oxidation of Isoeugenol to Vanillin with Copper Oxide Doped Reduced Graphene Oxide, ***Chemistry Select*** **2017**, 2, 3129 – 3136, (ISSN: 2365-6549), IF= waiting.

PATENTS:

A process for producing aromatic carboxylic acids by oxidation of methyl arenes. Indian Pat. Appl. (2014), IN 2013DE01346, Basudeb Saha, Sasanka Deka, Dinesh Gupta, Kalyan Jyoti Deori

CONFERENCE/WORKSHOP PARTICIPATED:

I have attended a large no. of conferences & workshops, some of which are mentioned below-

1. 5th BARC-Material Symposium- December 9-13, 2014

2. 5th Asia Oceana Conferencein Green And Sustainable Chemistry-15-17th January 2015 NEW DELHI INDIA 2014, Oral Presention

3. Indo-German Workshop On, New Prespectives For Nano-Carriers In Biomedical Applications,14th January 2013, Department of Chemistry, University of Delhi.

4. 4th Indo-Italian Seminar on, "Green Chemistry and Natural Products" Department of Chemistry, University of Delhi on 17th November 2010.

5. 8th Technology Led Entrepreneurship Programmers, Human Resource Development Group (HRDG), Council of Scientific & Industrial Research(CSIR), Push, New Delhi, From 4th -18th July-2011 at CSIR-Indian Institute of Chemical Technology, Hyderabad.

6. Introduction of Gaussian: Theory and Practice, 17-21 December, 2012, Organized by Royal Chemical Society-Delhi University.

7.Workshop On Information Literacy and Competency, 14th March,2011.

8.Workshop, How to write for and Get Published in Scientific Journals and Publish Manuscripts, Conducted by Springer in collaboration with the Delhi University Library System, 23rd August 2012.

TECHNICAL SKILLS:

Origin,WinGX, Mercury, Chem-Draw, Microsoft, Gaussian software, MS-office pack, HTML, Corel, Material characterization software (PCW, XPowder and High Score Plus)

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Fathers Name	Mr. Banarasi Gupta
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DECLARATION:

I hereby declare that the above given information is true to the best of my knowledge and belief.

Date: 21/09/ 2017

Place: Delhi

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