中国科学院大连化学物理研究所

优秀博士后奖励基金申请表

申 请 人：Joby Sebastian

研 究 组：1508

学科专业：Biomass Conversion

合作导师：Dr. Zheng Mingyuan &

     Prof. Zhang Tao

填表日期：2016 年 11 月 5 日

中国科学院大连化学物理研究所制

姓　　名	Joby Sebastian	性　　别	Male
出生日期	1984-11-30	民　　族	Indian
学历/学位	Doctor	专业技术职务	/
毕业院校	Academy of Scientific and Innovative Research (AcSIR), India.	专　　业	Chemical Sciences
（拟）入站时间	2016-07-24	入站性质	■统招统分　　□在职人员
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学习简历	起止年月	所在单位/专业	所获学位
	2002-2005	Mahatma Gandhi University, Kerala, India/ Chemistry	Bachelor of Science
	2005-2007	Mahatma Gandhi University, Kerala, India/ Chemistry	Master of Science
	2008-2010	Cochin University of Science and Technology, Kerala, India/ Industrial Catalysis	Master of Technology
	2010-2015	Academy of Scientific and Innovative Research, India/ Chemical Sciences	Doctor of Philosophy

工作经历	起止年月	所在单位	职务
	NA	NA	NA

博士学位论文摘要	博士论文题目	Catalytic Activity Study of Double-Metal Cyanide Complexes for Biodegradable Polymers Synthesis	
	指导教师姓名	Prof. Dr. Darbha Srinivas CSIR-National Chemical Laboratory, Pune-411008, India	

	（限 800 字）
	The main objective of the thesis was to unravel the critical structural and compositional features of catalysts responsible for their activity and selectivity in polymers synthesis through structure-activity correlations. The studied biodegradable polymers (polycarbonates and hyperbranched polyesters) are commercially well-known and categorized as bulk and speciality chemicals. Lewis acidity, micro/meso porosity and surface hydrophobicity are the main features of Fe-Zn double metal catalyst (DMC) that favoured good activity and selectivity in hyperbranched polyesters synthesis. Catalyst crystal symmetry, Lewis acidity, complexing agent, halogen and alkali metal content are the decisive parameters that controlled activity of Co-Zn DMCs in polycarbonate synthesis. The attempted studies greatly contribute towards the rational design of efficient DMC catalysts for said polymers synthesis.

1、主持或参与项目情况：

序号	项目名称	项目来源	项目金额	起止年度	角色
	NA	NA	NA	NA	NA

2、论文发表情况：

序号	论文题目	期刊名	影响因子	发表年度/卷期/页码	排序
1	Factors influencing the catalytic activity of of Co-Zn double-metal cyanide complexes for alternating polymerization of epoxides and CO_2	Applied Catalysis A: General	4.012	2015, 506, 163-172	I[st]
2.	Structure-induced catalytic activity of Co-Zn double-metal cyanide complexes for terpolymerization of propylene oxide, cyclohexene oxide and CO_2	RSC Advances	3.289	2015, 5, 18196-18203	I[st]
3.	Effects of method of preparation on catalytic activity of Co-Zn double-metal cyanide catalysts for copolymerization of CO_2 and epoxide	Applied Catalysis A: General	4.012	2014, 482, 300-308	I[st]

入站前期科研情况简介

4.	Solid, double-metal cyanide catalysts for the synthesis of hyperbranched polyesters and aliphatic polycarbonates	Journal Chemical Sciences	1.085	2014, 126, 499-509	Ist
5.	Influence of of method of preparation of solid, double-metal cyanide complexes on their catalytic activity for synthesis of hyperbranched polymers	Applied Catalysis A: General	4.012	2013, 464, 51-60	Ist
6.	Novel application of a Fe-Zn double-metal cyanide catalyst in the synthesis of biodegradable, hyperbranched polymers	Chemical Communications	6.567	2011, 47, 10449-10451	Ist
7.	Double-metal catalyst design in CO_2/epoxide polymerization	Sustainable Polymers from Biomass, Wiley Book Chapter	----	------	Ist

3、专利情况：

序号	专利名称	授权/申请	授权/申请号	起始日期	排序
1.	Process for preparing hyperbranched polyesters	Council of Scientific and Industrial Research (CSIR), New Delhi, India	14/001,332 US 9,334,361 B2	2016-05-10	IInd

4、获奖情况：

序号	奖励名称	奖励等级	授奖单位	奖励年度	排序

	1.	Junior research fellowship	National	University Grant Commision (UGC) and Council of Scientific and Industrial Research (CISIR), New Delhi, India.	2010	217th
	2.	Best poster award	National	15th National workshop on catalysis, Chennai, India	2011	I[st]
	3.	International travel grant	National	Department of Science and Technology (DST), New Delhi, India	2012	I[st]
	博士后研究题目： Catalytic Conversion of Cellulosic Biomass into Polyols					

博士后工作的研究计划	（简述研究计划的可行性、先进性和创新性，理论和现实意义）

Introduction: Lignocellulosic biomass- the starting point of biorefinery concept- is majorly composed of cellulose (35-50%) and contributes 70-95% of the 56.8×10^9 tonnes/year of biomass produced globally. Cellulose is a polymeric network fundamentally constructed from end to end β-1,4-glycosidic bonds of glucose monomers. One-pot catalytic hydrolytic hydrogenation of cellulose into polyols symbolizes a potential entry point for the production commodity chemicals through biorefinery concept.[1] Among the various poylols, ethylene glycol (EG) and 1,2-propane glycol (1,2-PG) are gaining much scientific interest. The global consumption of EG is estimated to be 21 million ton/year. EG finds an ever increase demand in polyester and resins industries and an antifreeze in automotive industry.[2] 1,2-PG is a valuable chemical in the synthesis of pharmaceuticals, polymers, agriculture adjuvant, transportation fuel, antifreeze, etc..[3] Conventionally, both EG and 1,2-PG are produced by a two step process involving the epoxidation of petroleum derived ethylene and propylene respectively followed by its hydration.[2,3] A one-pot catalytic conversion of cellulose into EG and 1,2-PG is highly desirable from economic (reduces unit operations) and sustainable (environmentally friendly) viewpoint. The complex network of this reaction necessitates a deep understanding of the behavior of catalysts under specific conditions. Challenges are involved in developing more efficient catalyst systems (transforms the process parameters more amenable) to accelerate the hydrolysis of cellulose and to modulate the reaction pathway to desired polyols in high yields.

State of the Art: One-pot catalytic hydrolytic hydrogenation of cellulose involves hydrolysis of cellulose into glucose in the first step and hydrogenation of retro Aldol condensation products in the second step.[2,4] A combination of acidity which favors hydrolysis and hydrogenation sites which drives the succeeding step, are key points in catalyst design. A suitable synergy between these catalytic components makes the system highly efficient for the entire process. Although homogeneous, heterogeneous and a combination of both have been used for the reaction, a whole heterogeneous pathway is preferred from scale-up point of view. It has been documented that the high chemical stability of cellulose requires harsh reaction conditions which adversely affect the selectivity of the catalytic system. Successful reports of various catalysts systems flourished the literature from 2008 onwards.[4] This includes W_2C/AC, $Ni-W_2C/AC$, H_2WO_4-Raney Ni, H_2WO_4-Ru/AC, WO_3-Ru/AC, Sn-Ni/AC, SnO-Ni/AC, $La(OH)_3$-Ni/AC, etc..[2,5] A maximum yield of EG up to 75% was reported on Ni-W/SBA-15 catalyst and yield of 32.2% of 1,2-PG on SnO-Ni/AC catalyst using cellulose as the starting substrate at reaction conditions of 245°C and H_2 pressure of > 50 bar for 0.5 h.[2,5] A sole selectivity to desired product- which reduces the capital cost in separation processes-, under less severe process conditions- which reduces the operational costs during scale-up phase- is highly recommended. This requires an extended systematic scientific research on innovative catalyst systems and optimization studies.

Objective: To accomplish very high desired product yield (EG or 1,2-PG) in one-pot catalytic hydrolytic hydrogenation of cellulose in an efficient and economic way over stable catalyst systems showing future prospects of scale-up opportunities. |

Methodology

a) Catalyst Design: Catalyst for this reaction should be bifunctional. A combination of vanadium (V_2O_5, $VOSO_4$, $VOPO_4$, etc.) which favors the hydrolysis of cellulose to glucose and isomerization of glucose to fructose to drive the reaction towards 1,2-PG along with a hydrogenation catalyst (Ni, Ru, Pt, Ir, etc. supported on AC, SBA-15, Al_2O_3) will be tested for the reaction. A physical mixture of these two active components and their co-existence on single support will be scrutinized in detail to control the synergy between the two components towards a better selective catalyst.

b) Catalyst Characterization techniques: XRD (crystal structure), ICP (metal output), SEM (particle morphology), HRTEM (size, lattice fringes), TPR (reductive nature of the metal and metal surface area), FTIR (electronic properties), Raman (defect sites, metal-atom electronic properties), XPS (oxidation state, surface composition), TPD (contribution from support acidity/bascity) and N_2 physisorption (textural properties) would be used to characterize the catalysts.

c) Reaction Procedure: A batch high pressure and high temperature autoclave (100 ml) would be used in the reaction. Reaction conditions would be in the range of 180 - 245 °C, 10 - 50 bar H_2 for a period of 0.5-2 h. Promising catalysts will be subjected to a semi-continuous process.

d) Product Characterization: All the reaction products will be identified and quantified using high performance liquid chromatography (HPLC) and gas chromatography (GC) instruments. Structural confirmation of compounds will be achieved through GC-MS and NMR techniques.

e) Analysis of Catalytic Activity: The activity (cellulose conversion) and selectivity (polyol yield) of different catalysts will be investigated and compared under identical conditions. Caution would be taken in comparison to address composition, oxidation state and acidity of the catalysts. Stability of the catalyst after reaction would be analysed by above characterization techniques and by hot filtration method. Based on this, structure-activity correlations would be clearly and astutely constructed.

Benefits of the Project
- Biomass valorisation in an efficient, sustainable and economic pathway.
- Green synthetic approach, carbon credit and make in China process.
- Advancing the knowledge on polyol synthesis from biomass to provide a rationale for future works and mechanistic interpretations.
- Commercialisation opportunities may reduce China's dependence on global market.
- High impact publications and patents.

Time Frame of the Project

Plan	Months
Literature survey, material procurement.	2
Synthesis, characterization and structural elucidation of various catalysts.	4
Screening of catalysts and optimization studies.	12
Crucial reactions, catalyst recycle studies and characterization of used catalyst.	3
Data analysis, structure–activity correlations and manuscript preparation	3

References

(1) (a) Geboers, J. A.; Vyver, S. V.; OOms, R.; Beeck, B. O.; Jacobs, P. A.; Sels, B. F. *Catal. Sci. Technol.* **2011**, *1*, 714-726. (b) Rinaldi, R.; Schüth, F. *ChemSusChem.* **2009**, *2*, 1096-1107.

(2) Zheng, M.; Pang, J.; Wang, A.; Zhang, T. *Chinese J. Catal.* **2014**, *35*, 602-613.

(3) Sun, D.; Yamada, Y.; Sato, S.; Ueda, W. *Appl. Catal. B: Env.* **2016**, *193*, 75-92.

(4) Ji, N.; Zheng, M.; Wang, A.; Wang, H.; Wang, X.; Chen, J. G. *Angew. Chem. Intd. Ed.* **2008**, *47*, 8510-8513.

(5) (a) Sun, R.; Zheng, M.; Pang, J.; Liu, X.; Wnag, J.; Pan, X.; Wang, A.; Wang, X.; Zhang, T. *ACS Catal.* **2016**, *6*, 191-201. (b) Sun, R.; Wang, T; Zheng, M.; Deng, W.; Pang, J.; Wang, A.; Wang, X.; Zhang, T. *ACS Catal.* **2015**, *5*, 874-883.

本人承诺	本人承诺：申请表所填内容均真实可靠。对因虚报、伪造等行为引起的后果及法律责任均由本人承担。 本人签字：　　　　　　　　　　　　　　　　　　2016 年 11 月 5 日

博士后合作导师考核推荐表

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<tr><td>

对申请人学术水平、科研能力等方面的考核意见：

Joby Sebastian 在博士学习期间从事碳酸酯及树枝状聚酯的合成工作，研究了 Co-Zn、Fe-Zn 双金属氰化物催化剂的物化性质与催化行为之间的关系，取得了系列的研究进展，发表了 5 篇高质量学术研究论文，以及 1 篇书籍章节论文，体现出良好的科研能力和科技论文撰写能力。在他来到大连化物所开始从事博士后工作的初期，通过文献阅读并与导师讨论，能够很快地进入到新的研究领域，对将要开展的生物质催化转化制低碳多元醇的研究工作能够提出清晰的研究思路，实验方案具有较好的可行性，数据分析合理，具有优秀的科研素质。

Dr. Joby Sebastian achieved a series of progresses in the course of his doctoral study on Zn based bimetal catalysts for polymer synthesis. He published more than 5 high-quality papers, and 1 chapter paper before his coming to DICP. This evidently demonstrates his outstanding ability to do research as well as good writing skills in composing academic papers. At DICP as a post doctor, he smoothly switched to the study of biomass conversion, which is a new field for him, again showing us his excellent capability and great potential in working on scientific research.

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对申请人提出的研究计划的评价（如可行性、先进性、创新之处、理论和实用意义）：

申请人在对"生物质制乙二醇、丙二醇"文献的系统理解的基础上，在指导教师的指导下，提出了研究方案，研究思路清晰，研究方案和内容具有很好的可行性，研究结果将发展新型高效催化剂、深入理解过渡金属催化糖分子 C-C 选择性断键的反应机制具有积极的促进作用，研究具有很好的创新性。研究中获得的性能优良的催化剂将具有很好的实际应用价值。

On the basis of well understanding the results of frontier research in biomass conversion to EG and 1,2-PG, Dr. Joby Sebastian carried out the present proposal under the supervision of Dr. Zheng Mingyuan and Prof. Zhang Tao. The research approach is clear and the research plan is of high feasibility. The result of proposed study will contribute to exploring more effective catalysts for biomass conversion to glycols. Meanwhile, it will be helpful for probing into the mechanism of C-C bond breakage by the catalysis of transition metal species. The study will not only have novelty but also be of notable significance for practical application once high-efficiency catalysts are developed.

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推荐意见（是否同意推荐申请优秀博士后奖励基金）：

I agree to recommend **Joby Sebastian** to apply the Outstanding Postdoc foundation.

　　　　　　　合作导师签字

　　　　　　　　　　年　　　月　　　日

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