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研 究 组: 1508

学科专业: Biomass Conversion

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	NA	NA	NA
		Catalytic Activity Study of Double-Metal Cyanide Complexes for Biodegradable Polymers Synthesis	
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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.

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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}

	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					
			/	/		
	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
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	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	Ist
	3.	International travel grant	National	Department of Science and Technology (DST), New Delhi, India	2012	Ist
	Catalytic Conversion of Cellulosic Biomass into Polyols					

Introduction: Lignocellulosic biomass- the starting point of biorefinery concept- is majorly composed of cellulose (35-50%) and contributes 70-95% of the 56.8x10^9 tonnes/year of biomass produced globally. Cellulose is a polymeric network fundamentally constructed from end to end -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:

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

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Dr. Joby Sebastian achieved a series of progresses in the course of his doctoral study on Zn based
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