CATALYSIS FOR TRANSFORMING BIOMASS TO VALUE ADDED CHEMICALS

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Abstract Although fossil fuels will continue to be the prime energy source for next few years, its limited reserves and environmental impact drives us to initiate the transition to renewable and clean energy resources. Among various renewable energy options, biomass occupies a unique position because it is, (i) most abundant and carbon neutral, (ii) acts as energy collector and storage system, (iii) the only large-scale energy source, (iv) available at low capital cost and (v) source of various value added chemicals, befitting to the concept of 'Biorefinery'. This paper presents a summary of our recent work on catalyst and process development for conversion of biomass derived molecules such as glycerol, levulinic acid and furfural to the respective diols, ring lactones and heterocycles having applications in variety of sectors including fuel and commodity.
Keywords: Biorefinery, catalytic, hydrogenation, bioglycerol, levulinic acid, propanediol,

1. Introduction

Crude oil which is non-regenerative has been serving as a prime feed stock for about a century for fuel and synthetic materials of the modern society. A paradigm shift towards sustainability and reduction in carbon footprints evolved the concept of biorefinery based on utilization of renewable biomass feedstock for producing biofuels and chemicals, which has the potential for commercialization in near future [Rode et al. (2014)]. As shown in Fig. 1, 'Biorefinery' concept is very similar to the conventional petro-refinery that produces multiple fuels and products in an integrated complex, biomass transformation to value added chemicals is possible either chemically or biologically using microorganisms. The catalysts and the processes being used in petro-refinery are mainly for the selective functionalization of hydrocarbons. On the other hand, new catalyst systems and tandem approaches need to be designed for biorefinery applications. This is because, biomass derived molecules are highly functionalized which demand selective removal of some functionalities with minimum number of steps from economic point of view. Biorefinery has several distinct advantages such as (i) lower net greenhouse gas generation (ii) bio-molecules such as carbohydrates invariably contain more than one oxygen atom hence, selective deoxygenation is necessary to obtain chemicals with less number of oxygen atoms. In the beginning of the 21st century, major attention was focused on new catalysts and routes for the conversion of several biobased platform molecules into fuels and multiple commodity products. Designing appropriate catalyst systems for selective deoxygenation of highly oxygenated bioderived molecules to platform chemicals and products is one of the most important challenges to realize the bio-refinery concept in near future. For economical and ethical reasons, anticipated large-scale production of biofuels will be possible from lignocellusic biomass. While more value added platform and specialty chemicals required in relatively low volumes can be obtained from functionalized sugars, vegetable oils and terpenes. Hence, developing catalysts and processes for high-value chemicals from biomass derived molecules is much more attractive commercially. However, due to the complex nature of biomass molecules as compared to simple hydrocarbons, selective formation of fine and platform molecules has proven much more demanding and troublesome

from technical consideration. The major solutions to such problems come from designing multifunctional catalysts aiming at tandem syntheses. In such approaches, reactor and process engineering innovations play an important role e.g. mass and heat transfer in case of multiphase reactions such as hydrogenation, for removal of the intermediate product formed and / or introduction of another reactant after commencement of the reaction, product separation and recovery etc. This paper summarizes our recent work on catalyst and laboratory scale process development exemplified by hydrodeoxygenation and / or hydrogenation of three important building blocks *viz.* glycerol, levulinic acid and furfural to the corresponding value-added diols, ring lactones and heterocyclic compounds.

Among these substrates, glycerol is the smallest, highly functionalized polyol and constitutes first as well as second generation biomass product as it is obtained as a by-product in (i) biodiesel production (ii) industrial conversion of lignocelluloses into ethanol and/or hydrogenolysis of sorbitol. The selective dehydration of glycerol and its subsequent hydrogenation (hydrodexygenation) gives two industrially important products *viz.* acetol and 1,2-propanediol (1,2-PDO), respectively, having industrial applications [Mane and Rode (2014)]. Similarly, levulinic acid sourced from cellulosic biomass is hydrogenated to a ring lactone *viz.* γ-valerolactone (GVL) having applications as a fuel additive and as a green solvent. After developing the catalysts and hydrogenation routes typically using an external hydrogen, we also successfully established the hydrogenation without using external hydrogen either by aqueous phase reforming (APR) or by transfer hydrogenation routes. In case of furfural as a substrate, its direct conversion of to tetrahydrofuran required Pd catalyst which involved the tandem route

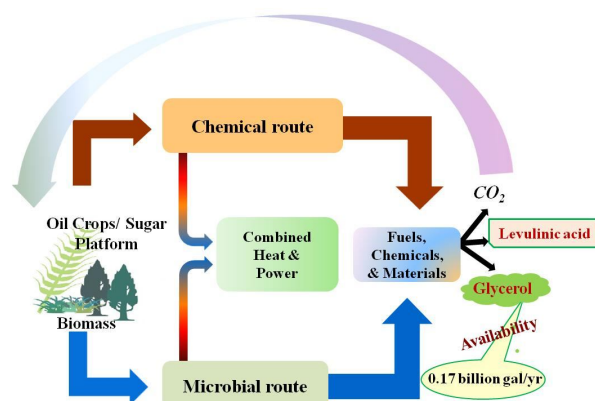comprising decarbonylation and hydrogenation reactions.

Figure 1. Biorefinery concept

2. Results and discussion

2.1. Dehydration and hydrogenolysis of aqueous glycerol

Among several value-added chemicals possible from glycerol, 1,2-propanediol (1,2-PDO) is one of the most important commercial product obtained by catalytic hydrogenolysis of glycerol. This transformation involves first step glycerol dehydration to acetol followed by its hydrogenation to 1,2-PDO (**Scheme 1**).
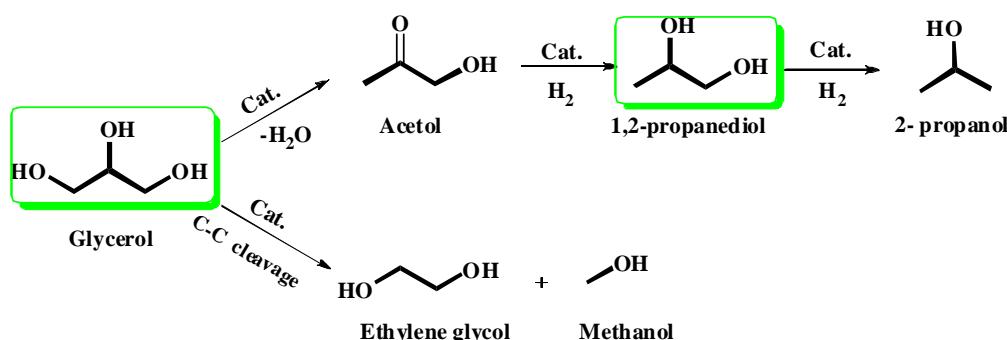
Scheme 1. Pathway for dehydration followed by hydrogenation of glycerol

The glycerol dehydration intermediate, acetol also has wide range applications in hydrogen production and pyruvaldehyde synthesis through oxidation and as a starting material in various organic transformations. Most of the studies on glycerol dehydration were mainly carried out in vapor phase at higher temperature in which the acetol selectivity was affected because of acrolein and other byproducts formation. These processes are also accompanied by fast catalyst deactivation due to extensive coke deposition. In our efforts, we developed Cat-2 and Cat-3 catalysts which gave acetol selectivity of 100% and 90% with glycerol conversion of 32 and 34%, respectively, in 2-propanol solvent. This is due to the highest acidity of these two catalysts (Table 1) as the glycerol dehydration is an acid catalyzed reaction. A detailed study of glycerol dehydration in aqueous medium was also carried out under inert atmosphere

Glycerol hydrogenolysis to 1,2-PDO has been largely exploited even for pilot and commercial scale trials over copper chromite catalysts. Due to the toxicity associated with Cr, we developed highly efficient non-chromium and non-noble nano Cu-Al catalyst, which was prepared by simple simultaneous co-precipitation digestion technique [Mane *et al.* (2010), Mane and Rode (2012)]. This new Cu-Al catalyst showed highest activity in both the solvents with the highest selectivity of 91% to 1,2-PDO for aqueous phase hydrogenolysis of glycerol in a very short reaction time of 5 h [Rode et al. (2014)]. The detail physico-chemical characterization of this catalysts revealed that the presence of stable particle size of 7–11 nm, inhibition of sintering of the active phase (Cu^0) due to presence of Cu_2O, as evidenced by

Table 1. Catalyst screening for glycerol dehydration to acetol

Catalysts	Acid strength (NH_3 mmole/g)	Conv. (%)	Selectivity (%)			
			Acetol	1,2-PDO	EG	Others
Cat-1 (Cu-Cr)	0.3414	37	86	14	-	-
Cat-2 (Cu-Cr-Al-Zn)	1.153	32	100	-	-	-
Cat-3(Cu-Cr-Al-Ba)	1.021	34	90	8	2	-
Cat-4(Cu-Cr-Zn)	0.7856	38	55	7	-	38

over Cu catalysts modified by oxides of different metals such as Al, Zn, Zr, Mg and Ba. Interestingly, only Al and Zr in combination with Cu showed excellent dehydration activity. It was concluded that glycerol dehydration to acetol needed both Bronsted as well as reduced Cu active sites [Mane et al. (2013)].

XRD and the higher acidity (1.567 mmol NH_3 g^{-1}) of Cu-Al catalyst were responsible for its higher activity for glycerol hydrogenolysis. As shown in Figure 1, this catalyst gave a TOS activity of 400 h for continuous hydrogenolysis of glycerol with an average glycerol conversion of 65% and >90%
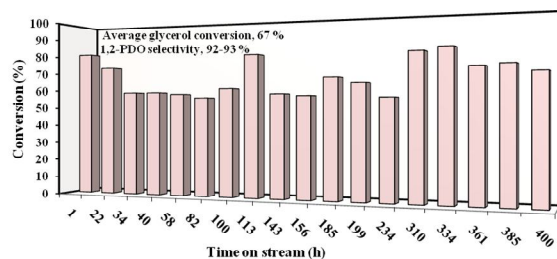

Figure 1. TOS of NCL catalyst for glycerol hydrogenolysis to 1,2-PDO

selectivity to 1,2-PDO [Mane and Rode (2013)]. The same catalyst was also effective for *in-situ* glycerol hydrogenolysis *via* aqueous phase glycerol reforming showing TOS of 400 h, due to its multifunctional sites [Mane and Rode (2012)].

The advantages of the NCL process are:

- Sustainable process for 1,2-PDO as it uses bio-derived glycerol as a feedstock
- Environmentally clean process as it doesnot produce byproducts which create effluent disposal problems
- Catalyst system composed of non-chromium, non-noble metals hence attractive process economics.
- Glycerol co-generated in bio-diesel process can be used with minimum pretreatment giving 1,2-PDO selectivity of > 75% with EG and lower alcohols, the later being volatile can be easily removed while the

product mix of 1,2-PDO and EG can be directly used as functional fluid.

Based on the continuous process operation results of NCL, complete mass balance across the reactor was done and the process economics has been also completed for a 25000 TPA 1,2-PDO production by Praj Ind. Downstream processing of the reactor crude has been proposed using the ASPEN PLUS Simulator, which involves three distillation columns. Water and acetol are mainly separated out in the first column along with the volatiles while the distillate of column 2, gives 1,2-PDO and EG under reduced pressure. 1,2-PDO (99.5%) is distilled out from column 3 leaving EG as the bottom product. Considering CAPEX and OPEX (including the feedstock cost and credit for EG), 1,2-PDO costing obtained was Rs. 69/kg. The project becomes more attractive particularly, for bio-glycerol cost < Rs. 45/kg considering 1, 2-PDO price of 90 Rs/kg and 100 crore capital investment. NCL proprietary catalyst is being prepared commercially by Sud-Chemie (India) which also showed the performance similar to the laboratory trials and the negotiations for commercialization of the process are in progress with some of the clients.

2.2 Hydrogenation of levulinic esters to γ-valerolactone (GVL)

A plethora of functionalized molecules can be derived from cellulosic biomass, which is available cheaply in large quantities all over the globe. Pacific Northwest National Laboratory (PNNL) and US National Renewable Energy Laboratory (NREL) have identified twelve such resource chemicals having potential industrial applications including chemical and fuel products [Gurbuz et al. (2011); Rode atl. (2014)]. Levulinic acid (LA) is one of the important compounds among these molecules for the biorefinery application. The commercial production of LA is offered by the well known Biofine process [Fitzpatrick (2006)]. This becomes a proven approach to convert cellulosic biomass to valuable platform chemicals, specifically levulinic acid (C6 fraction) and furfural (C5 fraction) with levulinic acid yield up to 70–80%, corresponding to 50% of the mass of the C6 sugars. The remaining mass is collected as formic acid (20%) and a solid residue called humins (30%), due to degradation of the large number of intermediates and lignin.

Catalytic hydrogenation of LA and its esters to γ-valerolactone (GVL) (Scheme 2) is of great commercial importance as GVL is the key product due to its benign properties and versatility with which it can be converted to downstream applications for the next generation fuel and fuel additives [Serrano-Ruiz *et al.* (2010)]. The subsequent hydrogenation product of GVL is pentanoic acid having most desirable applications as fuel/fuel additives [Lange et al. (2007)]. We have developed non noble metal nanocomposite catalysts comprising Cu and Zr for the first time for selective hydrogenation of levulinic acid and its methyl ester to GVL, the later is more advantageous due to (i) suppression of active metal leaching of hydrogenation catalyst caused by free carboxyl of levulinic acid and (ii) recyclability of alcohol formed during hydrogenation [Hengne and Rode, Green Chem. 2012]. HRTEM revealed the particle size of copper in a range of 10-14nm. Both XRD and Raman spectroscopy confirmed the formation of Cu-ZrO_2 nanocomposite and also the presence of mixed oxide phases along with Cu^0. Both the catalysts showed complete conversion of LA and its ester with >90% selectivity to GVL. Cu-ZrO_2 catalyst could be recycled efficiently for four times with almost no leaching of active metal, for LA hydrogenation in methanol.
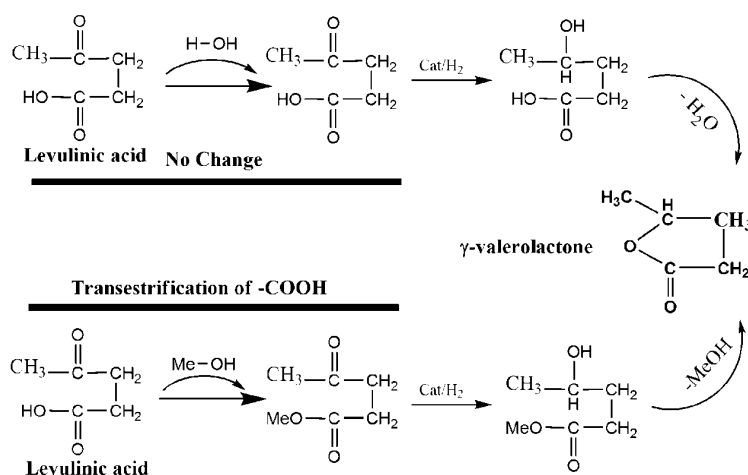
Scheme 2: Pathway of LA hydrogenation in water and in MeOH.

2.3 Furfural hydrogenation

Furfural (FFR) is another highly functionalized molecule obtained by acid hydrolysis of pentose sugars C5 (Xylose, arbinose) followed by dehydration. The catalytic hydrogenation of its side chain carbonyl and / or the ring gives an array of products such as furfuryl alcohol (FAL), tetrahydrofurfuryl alcohol (THFAL), 2-methylfuran (2-MF) and 2-methyl tetrahydrofuran (2-MTHF), useful in various applications. One of these products, THFAL is a 'green' industrial solvent due to its biodegradable nature. THFAL is conventionally produced by a two step catalytic hydrogenation of furfural (FFR) to furfuryl alcohol over Cu-Cr first and then its hydrogenation using noble metal catalysts separately. We have reported for the first time, direct selective hydrogenation of furfural to THFAL over Pd supported on MFI giving complete conversion of FFR [Biradar et al. (2014)]. Pd incorporation resulted in the transformation from mesoporous to microporous characteristic of structured MFI for achieving the highest selectivity to THFAL trough this direct pathway (Table 2). The silicalite crystals of MFI possessed hexagonal morphology with a flip structure matching with an orthorhombic symmetry of zeolite phase. The catalyst stability was demonstrated by its consistent performance up to four recycles.

Table 2. Catalyst screening for furfural hydrogenation

Sr. No.	Catalyst	Conversion %	Selectivity %					
			FAL	THFAL	MF	MTHF	THF	Other
1	3%Pd/MFI	93	31	67	--	--	2	--
2	3%Pd/SiO$_2$	76	50	31	--	--	--	19
3	3%Pd/SnMFI	72	49	30	1	--	2	6
4	3%Ru/MFI	100	79	13	2	--	--	3

5	3%Pd-3%Ru-MFI	98	29	49	4	1	3	5
6	3%Pd-20%Cu-MFI	100	91	--	--	--	--	--
7	3%Pd/MFI	84	SM	99	1	--	--	--

Reaction Conditions: Substrate, 5% (W/W); Solvent, Isopropyl alcohol (95 ml); Temperature, 493K; Pressure 500 psi; Agitation Speed, 1000 rpm; Catalyst, (3%Pd/MFI), 0.5 gm; Reaction time 5 h.

3 Summary and Conclusions

The rapid growth in glycerol availability from bio-diesel production and soap splitting as well as its highly functionalized nature makes the initiation point for developing new products and/or new routes for the existing fossil-derived products, from glycerol. Among these, 1, 2-PDO is an important commodity chemical obtained by hydrogenolysis of glycerol. With a global demand of 1.5 million tones/yr and an annual growth rate of 4% @ $ 1.6 / kg, 1,2-PDO is used in the production of antifreeze functional fluids, paints, humectants, and polyester resins. NCL team has successfully developed a highly efficient and stable, non-noble metal Cu based catalyst and a feasibility of bench scale continuous hydrogenolysis process for 1,2-PDO from glycerol, under NMITLI program. Laboratory scale (23 g catalyst) continuous process testing showed TOS of 500 h giving > 80% glycerol conversion with > 91% selectivity to 1,2-PDO. The major by-products formed were acetol and ethylene glycol. Feed tested was 60% aq. refined bio-glycerol procured from the international market. This process was further evaluated on a pilot scale (400 g catalyst) for TOS of 300 h with performance same as laboratory scale trials. For this purpose, catalyst preparation was also scaled up to 1 kg level at NCL and the catalyst was formulated in the form of 5 x 5 mm pellets. A protocol has been standardized for in-situ calcination and activation of the catalyst. Based on the continuous process operation results of NCL, complete mass balance across the reactor was done and the process economics has been also completed for a 25000 TPA 1,2-PDO production. Downstream processing of the reactor crude has been proposed using the ASPEN PLUS Simulator, which involves three distillation columns. MOU also has been signed with a catalyst manufacturer for commercial production of NCL proprietary catalyst and the catalyst evaluation trails are underway.

In another example, cellulosic biomass derived, levulinic acid was selectively hydrogenated to GVL, a fuel additive over another non-noble metal NCL proprietary catalyst. The metal leaching was completely suppressed when the hydrogenation was preceded by in-situ esterification of LA in presence of methanol. In case of direct hydrogenatin of furfural, the support modification was done by incorporation of the active metal function. Thus, the results of our work clearly highlight the techo-economic feasibility of catalytic routes for conversion of biomass derived molecules to value added products and establish the initial steps towards realization of biorefinery concept.

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