



Lignosulfonate-based macro/mesoporous solid protonic acids for acetalization of glycerol to bio-additives

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ABSTRACT

The enclosed paper introduces a novel, scalable and environmentally benign process for making strongly acidic solid meso/macroporous carbon catalysts from Na-lignosulfonate (LS), a byproduct from sulfite pulping. Ice-templated LS was converted to strongly acidic macro/mesoporous solid protonic acids via mild pyrolysis (350–450 °C) and ion/H⁺ exchanging technique. The synthesized materials were extensively characterized by FT-IR, Raman, XRD, XPS, TGA, FE-SEM, TEM and N₂-physisorption methods. These LS derived materials exhibited a macro/mesoporous and highly functionalized heteroatom doped (O, S) carbon structure with large amounts of surface –OH, –COOH and –SO₃H groups similar to the sulfonated carbon materials. Further, these carbon materials showed excellent potential as solid acid catalysts upon acetalization of glycerol with various bio-based aldehydes and ketones (acetone, methyl levulinate and furfural), easily outperforming the commercial acid exchange resins (Amberlite® IR120 and Amberlyst® 70). Most importantly, the optimum LS catalyst exhibiting a large specific surface area demonstrated exceptional potential for continuous solketal production (liquid phase atmospheric pressure operation) maintaining its activity (glycerol conversion ≥ 91%) and structural features even after 90 h time on stream.

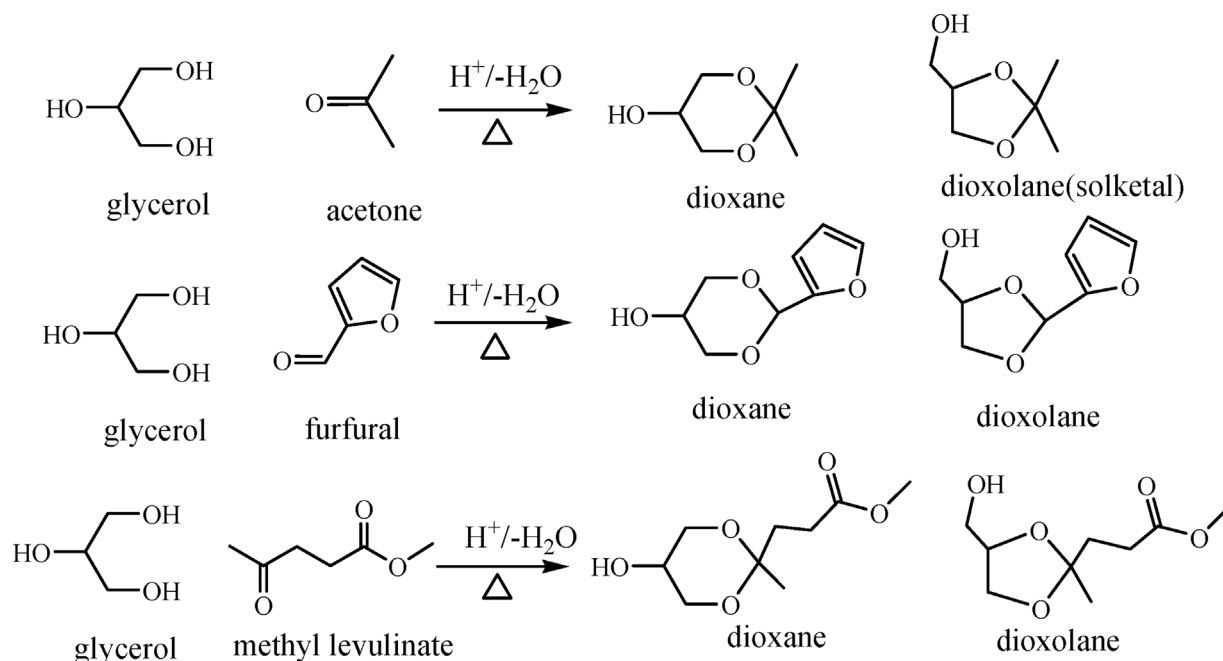
1. Introduction

Lignosulfonate or sulfonated lignin (LS) is a side-product from the production of wood pulp through sulfite pulping. Chemically this type of lignins represent a group of water soluble anionic polyelectrolyte polymers recovered from the spent sulfite pulping liquids (black liquor) containing large amounts of sulfonic groups at aliphatic carbons linked via C–S bonds, which roughly translate to 5–6% S in their dry form [1]. During the past few years LS has found wide variety applications in fields such as plasticizers upon concrete manufacture, dispersants in the oil drilling mud, modifiers in polymers, feedstock for producing plasterboard, corrosion inhibitors, flocculants and so on. Even so, in reality the scope of LS in the current market is limited to a handful of applications (cement industry, animal husbandry, mineral processing) and therefore sold in bulk, at low margins. The high level of S renders chemical processing of LS challenging, nonetheless it has been chemically processed into useful products such as dimethyl sulfide, dimethyl sulfoxide and vanillin [2–4]. On the other hand, the presence of naturally occurring –SO₃Na groups make LS an excellent raw material for

the synthesis of acidic catalysts and/or acid exchange materials through ion/H⁺ exchanging. The concept was recently demonstrated by several researchers, who utilized H⁺ exchanged LS as an alternative catalyst for various multicomponent reactions, such as one-pot synthesis of benzoxanthenes by a condensation reaction of dimedone with aldehyde and 2-naphthol and in sugar dehydration [5,6]. Regardless, such H⁺ exchanged LS are highly soluble in water and almost all protic solvents; therefore they require a multistep, complicated precipitation and regeneration cycle for reuse. H⁺ exchanged LS have also been heterogenized by phenol-formaldehyde type condensation reactions, in which the phenolic –OH groups present in LS are reacted with aldehydes in the presence of an acidic catalyst (usually HCl). These H⁺ exchanged phenol-formaldehyde type condensation products of LS have been employed as heterogeneous acid catalysts upon reactions such as hydroxyalkylation/alkylation and saccharification [7,8]. However, irrespective of their excellent properties as an acidic catalyst material, the aforementioned LS or LS based materials have several drawbacks such as poor thermal, mechanical and chemical stability, thus limiting their applicability as a solid catalysts. Also, they do not possess textural

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Scheme 1. Reaction scheme for acetalization of glycerol with acetone, furfural and methyl levulinate.

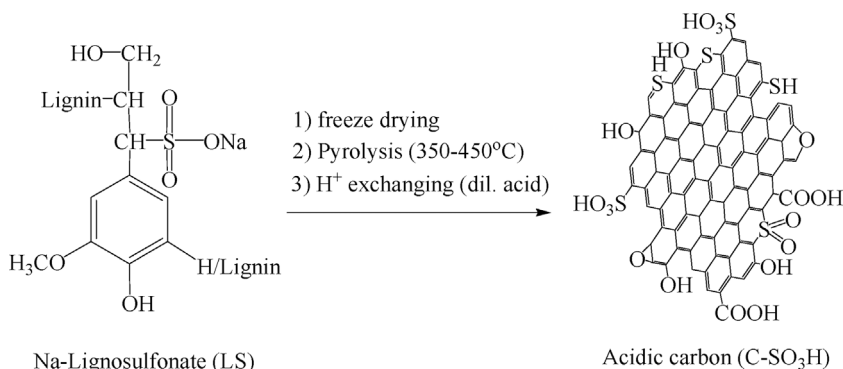
properties of an ideal heterogeneous catalyst such as high specific surface area, well defined porosity etc. Irrespective of this, the potential of LS as a sustainable solid acid catalyst precursor is undeniable. Considering their high carbon content, LS could also serve as an excellent platform for synthesizing versatile carbon materials (e.g. S doped or sulfonated carbon materials) [9].

Glycerol is the main by-product from biodiesel production by transesterification of triglycerides with methanol, corresponding to ca. 10 kg crude glycerol per 100 kg biodiesel produced. The flooding of additional glycerol stemming from biodiesel production into an already saturated market has adversely affected its market value in recent years. Thus, there have been significant efforts to find new applications and processes for glycerol valorization in order to stabilize the glycerol market and also to ensure the sustainability of the biodiesel production [10,11]. The acid catalyzed acetalization of glycerol with aldehydes or ketones is an important reaction for the synthesis of five (dioxolane) and six membered (dioxane) cyclic acetals/ketals (Scheme 1). These products have wide range of industrial applications and have been extensively utilized as solvents, fuel additives, low temperature heat-transfer fluids, surfactants, binders and so forth. In recent years there has been an increasing interest upon the acetalization of glycerol with bio-based carbonyl compounds (furfural, acetone, levulinic acid etc.) which yields renewable bio-additives. Among these, the five membered solketal produced by reacting glycerol with acetone has gained considerable attention as a multicomponent fuel additive in gasoline [12],

diesel [13] as well as biodiesel [14] formulations. Solketal synthesis has been investigated over a range of homogeneous as well heterogeneous catalysts including sulfuric acid, *p*-toluenesulfonic acid, aluminosilicates (zeolites, modified SBA-15) [15], mixed oxides ($\text{SO}_4^{2-}/\text{ZrO}_2$, supported SnO_2) [16,17], heteropolyacids [18], sulphonic ion exchange resin [19,20] and sulfonated carbons [21].

Among the investigated catalysts, the sulphonic ion exchange resins (Amberlyst® 15 Purolite® PD206, Amberlyst® 36) have been found to be the most efficient and have even been applied in continuous solketal production [22–24]. Nevertheless, these ion exchange catalysts tend to be expensive and are also prone to deactivation (due to H_2O accumulation and leaching) within short periods of time (ca. after 20–24 h on time on stream) [20,22,23]. In addition, most of the reported continuous processes operate at elevated pressures 27–120 bar, leading to increased operational and investment costs [20]. All these factors render the scale-up of an ion exchange resins based process from laboratory to industrial scale difficult. In this regard, LS could be an interesting raw material for the development of an inexpensive and stable heterogeneous catalyst for continuous solketal production.

Keeping the above in mind, the current study was undertaken with the aim of developing a porous, acidic and robust solid catalyst from LS. A novel, environmentally benign method based on ice-templating [25], mild pyrolysis (350–450 °C) and H^+ exchanging of LS was developed; whereby the need of sulfonation step with hazardous sulfonating agents such as conc./fuming H_2SO_4 , 4-benzenediazoniumsulfonate, ClHSO_4 etc.



Scheme 2. Method for preparing sulfonic acid functionalized carbon materials from LS.

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