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ARTICLE TYPE

Carbonized glycerol nano tubes as efficient catalysts for biofuel Production†

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Highly acid functionalized carbonized glycerol nanotubes successfully synthesized by a simultaneous carbonization and acidification have been identified as efficient and stable solid acid catalysts for biofuel production from glycerol and levulinic acid

Heterogenation of homogeneous catalysts is recently gaining importance to take advantage of higher pKa values of liquid catalysts along with the easy-to-seperate, energy-saving, non-corrosive nature of solid catalysts. Acid or base treatment of a carbon source is generally used for the production of functionalized materials. While, alkali activated carbon exhibiting excellent properties has been successfully prepared earlier from wood sources[1], the acid functionalization is gaining importance recently due to its applications in acid catalysis. Sulfonation of active carbon is one classic example of this category, where, the carbon sourcing organic compounds are treated with concentrated sulphuric acid so as to functionalize $-SO_3H$ (acidic) groups on the organic moiety to prepare solid acid catalysts suitable for various hydrocarbon conversions. Earlier Hara and co-workers[2] described the synthesis of carbon-based acid catalyst consists of poly aromatic carbon sheets obtained from sulfonation of naphthalene. Later, variety of organic molecules such as glucose and sucrose have been identified as suitable source for the preparation of solid acid catalysts.[3–5] Various carbon composite materials possessing porosity and acidity have been synthesized and explored for acid catalysis. [6-10] Recently, the acid functionalized carbon catalysts prepared from aromatic hydrocarbons, carbohydrates and glycerol were observed to be promising materials for the production of biodiesel.[11-18] Sulfonation was also employed as effective tool for the acid functionalization of mixed oxides such as niobium oxide.[19] Very recently, the waste sea food derived Chitin was successfully converted for the production of mesoporous nitrogen-containing carbon useful for the removal of heavy metals and for the production of nitrogen-rich chemicals. [20, 21] A cheper vegetable oil asphalt was also successfully employed for the preparation of a sulfonated carbon-based catalyst useful for biodiesel synthesis. Coaltar is the another low value material obtain from the fossil fuels that was also effectively utilized for the production of solid acid catalyst.[22] In the present scenario of processing of renewable sources for fuel prodcuion, the bio-char, a by-product obtain during bio-fuel production has proven to be a promising raw material for the production of activated carbon because of its availability at a low price.[23] The bottom line that determines the suitabilityof such materials for industrial applications is achieving good number of strong acid sites which are stable even at the reaction and regeneration condtions.

Density and strength of the acid sites on the solid surface plays vital role for catalytic applicaitons. The chemistry of acid functionalizaiotn of organic compound involves the carbonization of the organic compound so as to obtain poly cyclic organic molecule acts as carbon support, followed by its acid functionalization in which the $-OH$ groups of the support are replaced by acidic $-SO_3H$ groups. The main limitation of this process is in obtaining high acid density on the carbon-rich support, because, the carbonization of organic compounds lead to the formation of carbon-rich support bearing very few $-OH$ groups available for the acid functionalization. Due to this reason, most of the acid-funcitnalized organic molecules produced the solid acid catalysts with relatively lower activity towards acid catalyzed reactions. The procedure involve several preparation steps and also yields low acid density. [24,25]

The present work addresses the concept of facilitating molecular level interaction between carbon and acid group even before the complete carbonization of the substrate glycerol so as to get higher numbr of acid bearing groups. The concept was practically realized by a simple one-step carbonization of low value glycerol in presence of sulphuric acid to produce highly acid functionalized carbonized glycerol nano tubes posesseing hydrophobic carbon moiety with hydrophilic $-SO_3H$, $-OH$ and $-COOH$ groups exhibiting the scope for further functionalization with acid or metal ions along with good mechanical and thermal stability suitable for catalytic applications.

Herein we used glycerol as a cheaper and green carbon precursor alternative to the commonly used high cost resins, ionic surfactants and PEG.[9] In order to avoid the limitations involved in functionalization of organic moiety in two step partial carbonization and sulfonation methods reported in known prior art,[9,10] herein we adopted synthesis approach of simultaneous carbonization and sulfonation in a single step. The synthesis involves drop by drop addition of 60 g of 36N sulphuric acid (98% pure, Merk) to 20 g of glycerol (anhydrous, 99% pure, Merk) followed by treatment of the resultant mixture at 100°C for 24 h. Then the temperature is further raised to 180°C to form a viscous gel. At this stage N_2 gas is introduced as a careerer and the temperature is further increased to 300°C (ESI†) to facilitate the carbonization and transformation of the glycerol to hydrophobic carbon residue (~ 4.8 g) bearing sulfonyl groups.

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The low (Fig 1a) and wide angle (Fig. 1b) XRD patterns of the sample shows the amorphous and mesoporous nature of the material. The sharp diffraction band below 1°θ (Fig 1a) represents the presence of ordered mesopores. The IR spectra of the sample (Fig. 1c) shows broad band centered around 3,400 cm^{-1} due to OH stretching along with two bands at around 2929 cm^{-1} and 2860 cm^{-1} due to C–H stretching. The band around 1715 cm^{-1} due to -C=O stretching and the one at 1606 cm^{-1} due to -OH bending were also observed. The peak related to -SO$_3$H stretching and O=S=O stretching are appeared at -1207 cm^{-1} and 1040 cm^{-1} respectively. The morphology and internal structure of the sample is measured by SEM and TEM. The SEM image (Fig 1, ESI) indicates porous and rough surface of the amorphous material, while a clear cut image of bundles of nano tubes was appered in TEM images (Fig S2, ESI). The HRTEM (Fig 2d) shows the presence of 12 to 33 nm long tubes with 3 to 8 nm thickness. Overall, the TEM images indicate the formation of nano tubes of the carbonized glycerol apper as groups of bundles.

The thermal stability of the material was determined by TGA analysis (Fig. 3a) which shows the initial weight loss at three places; about 7 % weight loss below 190 °C, 2. 3 % weight loss between 190°C- 280°C and 30 % weight loss above 280°C which can be ascribed to the removal of water/moisture, weekly stable carbon moiety and carbon material respectively. The high moisture and water content is due to the presence of hydrophilic groups in the materials. Overall, the TGA analysis suggests that the catalyst is thermally stable to work at the chosen reaction temperature i.e 103°C under solvent free conditions.

The XPS spectra C 1s of the sample shown in Fig. 4 exhibits three main components that can be assigned as binding energy of 282.6 eV for chemisorbed carbon[27], 284.7 eV and 285.8 for sp^2 (C-C) and sp^3 (C-H)[28] and 288.9 for COOH[29] respectively. The relative concentration of sp2 and sp3 carbon in the sample was found to be 61 % and 32 % respectively, indicates the dominant presence of SP^2 carbon.

The EDX analysis of the material shows the presence of carbon, sulphur and oxygen (Fig 2, ESI). The elemental analysis data indicate major amount of Carbon (> 60%) along with sulphur and hydrogen (Table 1) representing the carbon interacted –SO$_3$H groups. The total acidity of the samples measured by titration method observed to be 4.03 mmol/g that makes the material suitable for acid catalyzed reactions. The contribution of -SO$_3$H to the total acidity was determined by sulphur equivalent of -SO$_3$H from elemental analysis which is 1.43 mmol/g. The difference in total acidity and -SO$_3$H acidity comes to be 2.6 mmol/g which is due to combined contribution of -COOH and -OH groups. These carboxylic and phenolic groups are expected to be formed during sulfonation of the glycerol when treatment is conducted in open air where some carbon moiety can be oxidized to give phenolic -OH and -COOH groups in presence of strong sulphuric acid.
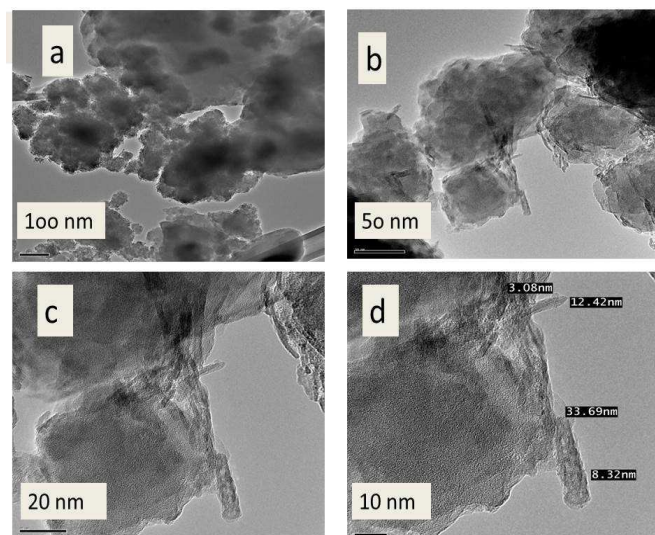
Table 1. Elemental composition and acidic property of synthesized glycerol carbonized nanotubes

Entry	Carbon (%)	Hydrogen (%)	Sulfur (%)	Acid by –SO$_3$H (mmol/g)	Total acidity (mmol/g)
1	62.67	2.95	1.11	0.93	3.67
2	69.02	3.22	1.00	0.92	3.66

Carbon, Hydrogen and Sulfur measured by CHNS analyzer, Total acidity measured by titration method, while the acidity due to –SO$_3$H is calculated from the S equivalent.
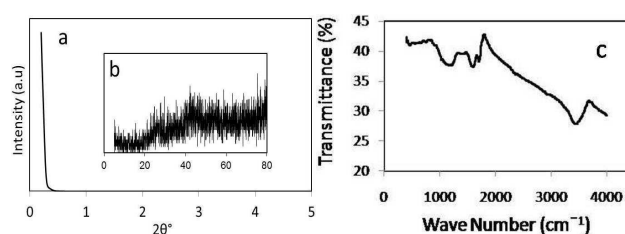
Fig. 1a and 1b are low and wide angle XRD patterns, Fig 1c is the FTIR spectra of the sunthesized material

Fig. 2 TEM and HRTEM images of material
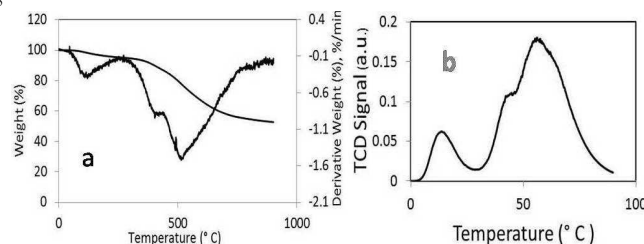
Fig. 3a is TG/DTA and 3b is NH$_3$ TPD of the synthesized material

Fig. 4 XPS spectra of the synthesized carbon nano tubes

Acid functionalized carbonized nanotubes of glycerol

Fig. 5 Scematic representation for the formation of nanotubes from glycerol carbonization

Unlike the other reported methods, the present method effectively produced the nano tube morphology. The simultaneous sulfonation adopt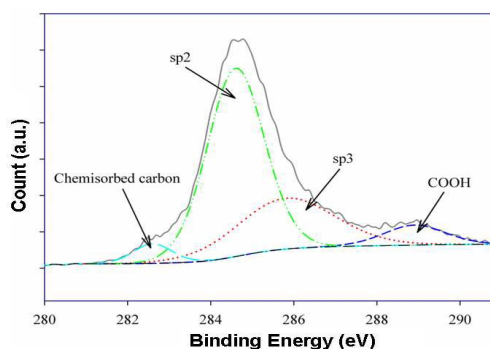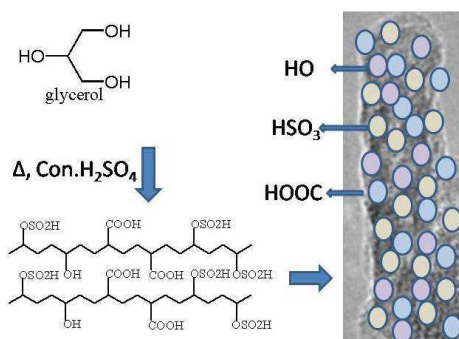ed right from the beginning of the carbonization of the carbon source (glycerol) of the present study seems to be responsible for the formation of nano tubes as preferred morphology. Here the polar –SO_3H groups initially present on the molecular level carbon moiety are believed to facilitate the interaction among such species to form nano particles, followed by their further interaction in the course of extended carbonization and sulfonation to form nano sheets, and the eventual edge side interaction of the sheets (roling of the sheets) thus can result in the formation of nano tubes. Here the presence of polar –SO3H, -OH and –COOH groups seem to facilitate the cross bonding in the nano sheets to initiate roling and for the formation of nano tubes. Based on the physic-chemical properties of the synthesized material, a schematic representation for the formation of acid functionalized nano tubes from glycerol is shown in Fig 5. The resultant material bearing high amount of hydrophillic –OH, –COOH and –SO_3H groups on its surface gives better activity because these groups are supposed to have better interaction with hydrophilic reactants used in biofuel production. In the present study we have considered two important reactions to evaluate the catalyst performance, namely, acetalation of glycerol (a low value bio-waste) to produce solketal and esterification of renewable levulinic aicd to produce n-butyl levulinate. Both the proucts are high quality oxygenates used as bio-diesel additives.

The properties of glycerol such as diesel-immiscibility make it not suitable even for fuel blending and research is on for value addition of glycerol through its chemical conversion to useful products and to find new applications for this cheap and off grade glycerol obtained from biodiesel plants. Wide variety of chemicals and fuel blending stocks were reported to produce from glycerol through the chemical reactions, but, the production of oxygenates from glycerol gains much importance due to the excellent diesel-blending property of the oxygenates that not only improve the quality of the fuel but also increases the overall yield of the biodiesel in helping to meet the target for energy production from renewable sources for transport in the energy utilization directive.[11-18] Acetalization with ketones, especially acetone is gaining importance due to the fact that acetone is widely produced from biomass conversion as well as from the chemical process of cumene cracking. Hence, facilitating reaction between two biomass derived products glycerol and acetone is advantageous as they constitute an excellent component for the formulation of gasoline, diesel and biodiesel fuels.

Table 2. Performance evalution in solketal production

Entry	Reaction Time (h)	Glycerol Conversion (wt %)	Solketal Selectivity (%)
1	1/2	90	100
2	2	94	100
3	4	85	100
4	6	87	100
5	8	85	100
6*	2	92	100

Reaction Condition:Temperature=70°C, Catalyst=650 mg, glycerol :acetone=1:6 molar ratio at solvent-free conditions
* the data obtained on the catalyst after 4 reaction cycles

Table 3. Performance in Butyl Levulinate Production

Entry	Reaction Time (h)	LevulinicAcid Conversion (wt%)	Butyl Levulinate Selectivity (%)
1	4	70	100
2	4	80	100
3	4	85	100
4	8	91	100
5	10	90	100

Reaction Condition:For entry1 Temperature=70°C, entry 2 T = 100°C and entry 3 to 5, T = 120°C, while the other conditions are same. Catalyst=650 mg, Levulinic acid: n-Butanol = 1:1 molar ratio

Carbohydrates derived from biomass are great source for the production of bio-based platform molecules, In particular levulinic acid (4-oxo pentanoic acid) derived from the carbohydrates is an important intermediate that needs to be converted into valuable products. Esterificatin of levulinic acid with alcohols is an efficient way for the value addition as the resultant levunates are excellent bio-diesel additive properties.[26]

The material synthesized in the present study exhibiting strong acidity with polar functional groups on the surface is expected to be suitable for the acetalation of glycerol and esterification of levulinic acid. As shown in table 2, the material exhibited promising catalytic activity in solvent free liquid phase acetalation reaction in Parr reactor at 70°C in the short reaction time of half an hour. The highest conversion of 94% is achieved after 2 h reaction time while the selectivity to solketal is always 100%. The performances of the catalyst is not directly correlated with the amount of sulphur estimated by elemental analysis. This may be due to the contribution of -COOH and phenolic -OH groups (in addition to -SO_3H) to the total acidity. Further, the co-presence of the hydrophilic –COOH and phenolic –OH groups in the material seems to play an important role in promoting the activity of the catalyst by creating strong affinity between the hydrophilic parts of the reactants with the catalyst. The catalyst also exhibited constant glycerol conversion up to the 4 reaction cycles (Table 2). The reusability of the catalyst synthesized in this work was investigated by filtering the reaction solution, washing with ethanol and drying the catalyst material at 120°C between consecutive cycles. The performance of catalyst was observed to be comparable with the fresh catalyst even after 4 reaction cycles (entry 6, table 2) supports the stability in active sites on the catalyst. This aspect was further confirmed from the spent catalyst analysis. The XRD, FTIR and TG/DTA spectra of the spent catalyst compares well with the fresh one (Fig S3, S4, S5, ESI), indicates the structure was protected during the reaction. The TPD analysis also indicates comparable acidity remains present on the spent catalyst, except a little increase in the low temperature peak related to the weak acidity (Fig S6,

ESI). A little increase in the SP^3 carbon and –COOH groups was observed in XPS of the spent catalyst (Fig S&, ESI) perhaps due to the oxidation of some carbon in SP^2 state to bear extra –COOH groups at reaction conditions. This is in consistant with the relatively higher weak acid sites observed in TPD of the spent catalyst. Small amount of an additional component related to C-N was also appeared at 287.5 eV in the spent catalyst.[30] But, these changes do not influenced the activity of the spent catalyst.

The catalyst also exhibited good activity towards esterification reaction of levulinic acid with butanol (Table 3). The levulinic acid conversion is ~70% at 70°C and increased with the reaction temperature up to 120°C. The highest conversion of 91% levulinic acid was obtained at 120°C after 8 h reaction time. The selectivity towards n-butyl levulinate is always 100% that makes the product useful for fuel applications.

In conclusion, the present communication demonstrates a facile and efficient carbonization-acidification of bio-waste glycerol to produce high acid-bearing carbonized nanotubes of glycerol that can catalyze important reactions such as acetalization of glycerol and esterificaitn of levulinic acid to produce valuable bio-fuel suitable for blending applications. Moreover, the active material does not suffer from leaching problems and can be efficiently reused in consecutive catalytic cycles.

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Graphical abstract

Carbonized glycerol nano tubes as efficient catalysts for biofuel Production†

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Highly acid functionalized carbonized glycerol nano tubes obtained by a simple, single step carbonization acted as an efficient and stable solid acid catalyst for acetalization of glycerol and esterification of levulinic acid to produce biofuel