Appendix I

Synthesis of GTBE over DOWC based sulfonated AC

The catalytic applicability of the DOWC derived sulfonated carbons were examined in glycerol upgradation to fuel additives (GTBE) by etherification with tert-butanol (TBA).

A1.1. Introduction

Glycerol is an unavoidable by-product from biodiesel and soap production, although it cannot be used as a fuel or additive it can be etherified with tert-butyl alcohol (TBA) or isobutene in the presence of acid catalysts to mono-tertbutyl glycerol (MTBG), di-tert-butyl glycerol (DTBG), and tri-tert-butyl-glycerol (TTBG) ethers (collectively called as GTBE). Glycerol etherification with tert-butanol produces water as a by-product, while isobutene does not. Conversely, isobutene is very expensive compared to tert-butanol and requires high pressure (2 MPa) to keep it in liquid form. Klepacova et al. [1,4] applied several commercial solid acid catalysts such as Amberlysts (15, 31, 35 and 119), ion-exchange resins (A-31 and A-119) and large-pore zeolites (H-Y and H-Beta) to catalyze glycerol etherification with isobutene and tert-butanol and found that etherification with tert-butanol leads to lower conversion and selectivity owing to formation of water by dehydration of tert-butanol, deactivating the catalysts. Overall, etherification with TBA is more attractive due to lower costs and operational difficulties associated with handling highly inflammable isobutene [1-6].

Owing to their remarkable acidic properties the sulfonated carbons or sugar catalysts may have prospective catalytic applications in glycerol etherification. They have already been applied in a range of acid catalyzed reactions such as: esterification, transesterification, and hydrolysis. Recently, these sulfonic acid-functionalized carbon materials have also been demonstrated to show excellent catalytic activity in glycerol transformations (esterification and etherification), however, the etherification with isobutene showed more favorable results with better selectivity towards desired higher ethers [7-9]. Thus keeping in mind the role of sulfonated carbons in glycerol conversion, the etherification activity of the synthesized DOWC based sulfonated carbons were also evaluated using PS500 as one of the representative catalysts.
A1.2. Materials and methods

A1.2.1. Materials

Glycerol (99%, anhydrous), tert-Butanol (ACS grade) were purchased from Merck India Ltd. N,O-Bis(trimethylsilyl)trifluoroacetamide (99%), Pyridine (99%) and all analytical solvents were purchased from Sigma Aldrich. The PACS described in Chapter 6 was chosen as representative catalyst due to highest surface and acidity among the DOWC based sulfonated carbons.

A1.2.2. Methods

The catalytic tests were performed in batch mode in a 200 mL autoclave equipped with digital temperature indicator and magnetic stirring. In a typical reaction, 0.5 g (5 wt%) of catalyst (particle size <250 µm, pre dried at 150 °C) was added to 10 g glycerol stirred (250 rpm), followed by an addition of 32.2/73 g preheated tert-butanol, heated to 90 °C for desired time (1-10 h). After, completion of reaction to determine conversion of glycerol, products were analysed by GC on a TRACE™ 1300 (Thermo Scientific) equipped with FID detector and Agilent (Select Biodiesel for glycerides) GC column. The column temperature was held at 50 °C hold 1 minute, 15 °C/minute to 180 °C, 7 °C/minute to 230 °C, 30 °C/minute to 380 °C and held for 5 minute. Helium was used as the carrier gas at a flow rate of 3 mL/min. The products were subjected to silylation prior to GC analysis. In a typical process 500 mg N,O-Bis(trimethylsilyl)trifluoroacetamide was added to 100 mg product followed by addition of 10 mL pyridine, the resulting contents were haled on a oil bath at 70 °C for 1 h. The individual products were identified by GC-MS of un-silylated products due to commercial unavailability standards. GC-MS was performed on a on a Perkin Elmer Claurus 600 equipped with DB-5 MS column to achieve desired chromatographic separation. The column temperature was held at 50 °C for 1 min, then heated from 50 °C to 250 °C and the rate of increase was 5 °C/min. The carrier gas used was helium and the flow rate was maintained at 1 mL/min. The MS was scanned from 50 to 600 Da. The conversion $C_{gly}$ was based on glycerol concentration measured at specified time intervals from calibration curves:

$$C_{gly}(\%) = \frac{(C_i - C_t)}{C_i} \quad (A. i)$$

where, $C_i$ is the initial concentration and $C_t$ is concentration measured at time t.
Here, the selectivity to MTBG, DTBG and TTBG has been expressed as area percentages from TIC (total ion chromatogram) of GC-MS as direct comparison with standard solutions of MTBG, DTBGs and TTBG was not possible.

**A1.3. Results and discussion**

Fig. A11-A14, shows the TIC and EI mass spectrum of the sample obtained at 4 h. The product identification was based on the method described by Jamróz et al. [10]. Almost all EI spectra were very similar to each other, typically exhibiting the base peak at m/z = 57 corresponding to fragment ion [C₄H₉]⁺ of TBA. These spectra are slightly different from the ones report by Janaun et al. [8] where peak at m/z = 45 corresponding to fragment ion [C₃H₉]⁺ from -(CH₃)₃, was dominant. Most of the EI patterns resembled those reported by Jamroz et al. [10], where peak the base peak was at m/z = 57.

![Gas chromatogram of the sample obtained at 4 h.](image)

Figure A11. Gas chromatogram of the sample obtained at 4 h.
Figure AI2. EI mass spectrum of (a) TBA and (b) TTBG
Figure AI3. EI mass spectrum of (a) DTBG and (b) DTBG isomer.
Figure AI4. EI mass spectrum of (a) MTBG and (b) MTBG isomer.
Fig. AI5 shows the catalytic activity of PACS at 90 °C as function of glycerol conversion. Conversion increased with increased reaction time and reached a steady equilibrium (94%) at 6 h, however selectivity to higher ethers (di- and tri-) steadily increased till 7 h (expressed as area percentage) beyond which it remained constant. In comparison to similar agro-industrial waste based carbons reported in literature the selectivity to higher ethers were lower most likely from the use of lower reaction temperature [7,11]. However, the improved conversion could be associated with the higher surface area of JACS (914 m$^2$/g) in comparison to those previously reported in literature (<1 m$^2$/g). On increasing molar ratio the selectivity to the di- ether increased but tri-ether selectivity did not increase significantly. Therefore, it might be possible to enhance the selectivity of higher ethers by (i) removal of water and/or (ii) increasing the reaction temperature considering the high thermal stability of the DOWC based sulfonated carbon materials.

![Graph AI.5](image)

Figure AI5. (a) Glycerol conversion as a function of reaction time and (b) effect of tert-butanol (TBA) to glycerol molar ratio on product selectivity. Reaction conditions: catalyst = 5 wt% of glycerol, temperature = 90 °C, time = 6 h, autogenous pressure and stirring rate = 500 rpm.
A1.4. Conclusion

The DOWC based sulfonated carbons can be employed as catalysts in glycerol upgradation into fuel additives (GTBE) by etherification with TBA. The higher surface area these materials facilitated improved conversions (>90%), however, selectivity to desired higher ethers DTBG and TTBG were low most likely from the low reaction temperatures. The future prospects of the study will be improving DTBG selectivity as conversion to TTBG results in unnecessary consumption of TBA, since DTBG has fuel properties comparable to TTBG. In addition, effect of reuse and comparison with commercial zeolites and sulfonated resins will also be studied.

A1.5. References


Appendix II

DCC aided grafting –NH₂ groups on active carbon

A green protocol for grafting carbon (AC) surfaces with –NH₂ groups was developed and applied on the Jatropha curcas DOWC derived AC. –NH₂ modification was achieved by N,N'-Dicyclohexylcarbodiimide (DCC) mediated grafting process.

AII.1. Introduction

Carbon materials have unique mechanical, electrical and structural properties which have due to which they find diverse applications in catalysis, adsorption, water, gas purification and as electrode materials. Furthermore, the surface properties of the carbon materials can be easily tuned to incorporate acidic or basic groups, which can alter their properties drastically [1]. The –SO₃H modified carbons have high acidities comparable to H₂SO₄ which makes them a suitable substitute to conc. H₂SO₄ acid catalyzed reactions [1-3]. In a similar way several methods are available to produce an amine-functionalized carbon surface, which may be used to form subsequent amide linkages, hydrogen bonds, or merely to change the surface adsorption properties [1,4]. Recently, Villa et al. [5] used amino-functionalized carbon nanotubes as solid basic catalysts for the transesterification of triglycerides. In addition such materials can find applications as adsorbents for CO₂ removal from biogas or industrial flue gases. So, far amination of the carbon surfaces is accomplished mainly by reaction with diamines. A typical process involving three steps, (i) introduction of carboxylic groups onto the surface of carbon by oxidising it with nitric acid, followed by (ii) reaction with thionyl chloride to transform the carboxylic acid groups to the acid chlorides which are than (iii) treated with diamines to yield amine modified carbons. Activation with thionyl chloride resulted in more diamine being immobilized on the surface than reaction with nitric acid alone. It has also been shown that carbon fibers oxidized with nitric acid can be functionalized with amine groups by reaction with tetraethylenepentamine. Both single and double-bridged forms were present on the carbon surface. Other methods include attachment by Attachment via. diazonium chemistry and n-butyllithium (nBuLi) activation methods [1,6-9].
With this prospect in mind an attempt was made to graft amines onto carbon surface by using N,N'-Dicyclohexylcarbodiimide (DCC) as a dehydrating/condensing agent to form amide bonds (Scheme A1). The uses of DCC can eliminate the use SOCl₂ and the number of steps involved in traditional amine grafting process (Scheme A2).

Scheme A1 Proposed route for -NH₂ grafting (N,N'-Dicyclohexylcarbodiimide aided)

Scheme A2 Conventional route for -NH₂ grafting (SOCl₂ aided)

AII.2. Materials and Methods

AII.2.1. Materials

Oil cake press from Jatropha Curcas seeds were collected, ground and passed through Standard ASTM sieve (Mesh No. 60, 0.25 mm) and used as a precursor for the preparation of AC. HNO₃ (70%), tetrahydrofuran (HPLC grade) and acetone (99.5%) were purchased from Merck India Ltd. Mumbai. N,N'-Dicyclohexylcarbodiimide (≥99%) and Ethylenediamine (≥99.5%) were purchased from Sigma Aldrich. All solvents and chemicals were used without further purifications.

The AC was prepared by chemical activation oil cake press with 50% phosphoric acid as at 500 °C under self-generated atmospheres as described earlier. For comparison unactivated carbon samples were also prepared at 500 °C as control.

AII.2.2. –NH₂ grafting

In a typical process, 5 g Jatropha Curcas derived AC was refluxed with 50 g concentrated HNO₃ for 4 h to generate –COOH groups on carbon surface. In the next step,
1 g –COOH modified carbon was refluxed with 0.33 mole (20 g) ethylenediamine (EDA) or hexaethylenediamine (HEDA) in the presence of 10 g N,N’-Dicyclohexylcarbodiimide (DCC) and 50 ml THF at 70 °C for 72 h. The resulting product was filtered washed with THF, acetone and then methanol until the filtrate became clear. The resulting amidized carbon were dried in vacuum at 110 °C for 24 h and labeled as NH$_2$-AC. The resulting materials were characterized by N$_2$-physisorption, XRD, elemental analysis and FT-IR.

AII.3. Results and discussion

The FT-IR spectrum of unmodified AC exhibit the typical bands of carbonyl groups (C=O, ~1712 cm$^{-1}$) and characteristic peaks of incompletely carbonised materials, near 1580 cm$^{-1}$ attributable to aromatic ring modes. Upon oxidation, the intensity of –COOH bands increased sharply, in agreement with the success of oxidation process resulting in introduction of abundant –COOH groups on AC surface. The successful grafting of –NH$_2$ on AC was evident from shifting of this carbonyl band at 1712 cm$^{-1}$ to 1569 cm$^{-1}$ which confirmed the formation of amide linkages (CO-NH bonds) between EDA and -COOH groups. The increased intensity of carbonyl band in HNO$_3$ treated carbons was (Fig. AII1). The success of surface modifications on carbon was also indicated by the acid site densities measured by titration methods. The –NH$_2$ densities were estimated to be 2.53 and 2.26 mmol/g for EDA and HDA grafted carbons respectively, based on elemental analysis. There was almost ~96-97% reduction in specific surface area following NH$_2$ modification probably due to excessive loading of such groups. Thus, future prospective exists for optimization of the grafting conditions in order to achieve higher –NH$_2$ density, specific surface area and porosity simultaneously. The loss of porosity was also visible in the TEM images (Fig. AII2). The XRD patterns (not shown) exhibit a similar broad and weak (002) diffraction peak near 2θ=15-30° and resembled the previously discussed amorphous carbons (Chapter 5 and 6). No, detectable changes in XRD patterns were observed upon surface modification.

Both EDA and HEDA modified carbons (NH$_2$-AC) showed negligible transesterification activity at methanol to oil molar ratio of 9:1 and 65 °C, the low activity could be attributed to the low basicity of the primary amine groups and the low specific
surface area of these materials restricting the interaction between larger triglyceride molecules with active sites. Nonetheless, it could be possible to improve transesterification activity upon (i) increasing reaction temperature (ii) by grafting more basic amines (secondary, tertiary or guanidines) and (iii) increasing catalyst surface area [6]. The prospective applications of current materials may include: as sorbent for removal of carbon dioxide (CO₂), arsenic from water and as electrodes.

Fig. AII.1. FT-IR patterns showing successful grafting of –NH₂ group

Fig. AII1. TEM images of (a) NH₂-AC (EDA) and (b) JAC showing loss of porosity upon grafting AC surface with ethylenediamine (EDA).
AII.4. Conclusion

Carbons with up to 14% N and –NH$_2$ group density of 2.4-2.5 mmol/g were obtained by DCC mediated grafting process. Use of DCC eliminates the use of SOCl$_2$ and reduces the number of steps involved. However, grafting also reduced porosity and surface area, thus, future prospective of the work will be optimization of the preparatory conditions to obtain high surface area, porosity and –NH$_2$ functionalization simultaneously.

AII.5. References


