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Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

Facile single step synthesis of acid functionalized nano porous carbon composite as efficient catalyst for tertiary butylation of phenol †Devaki Nandan^{ab} and Nagabhatla Viswanadham^{ab*}

DOI: 10.1039/b000000x

Here we report a simple synthesis method for the preparation of acid functionalized nano porous nano composite of carbon for the first time from petroleum waste by a simultaneous carbonisation and sulfonation method. The material exhibited highest ever reported catalytic activity towards liquid phase tertiary butylation of phenol up to the several reaction cycles

The combinatorial approach of immobilizing homogenous catalysts on to heterogeneous support has recently gained importance to get the advantage of high K_a values of homogenous catalysts and the easy-to-separate handling of the heterogeneous catalysts. But, such catalysts suffer from leaching out problem of weakly attached active sites on the support at the real reaction conditions.

Acid functionalization of solid materials such as sulfonation of active carbon and its composite materials is an interesting area of origin that aims to take advantage of higher K_a values of liquid acids and the non-corrosive, easy-to-separate property of solids for catalytic applications. The methods such as sulfonation of activated carbon resin and metallic oxide has come up to solve the problem of acid density, but the procedure is time consuming and involves several preparation steps.^{1,2} Moreover, the immobilization of acidic functional group is difficult and also yields low acid density. Further the usability of recyclable solid materials as replacement to homogeneous acid catalysts is usually limited due to the low density and strength of the acid sites on the solid surface.

Carbon based solid sulfonic acid catalysts were first described by Hara and co-workers.³ In their work, a carbon-based acid catalyst composed of small polycyclic aromatic carbon sheets with attached sulfonic acid groups ($-\text{SO}_3\text{H}$) was obtained by heating aromatic compounds (e.g., naphthalene) in concentrated sulphuric acid. Lately, they employed glucose and sucrose as a carbon precursor to prepare carbon-based sulfonic acid catalysts and investigated their catalytic properties.^{4–6} Composite sulfonated porous carbon materials were also synthesized and used as solid acid catalysts as well.^{7–11} Recent studies using sulfonated carbon-based acid catalysts prepared from aromatic hydrocarbons, carbohydrates and glycerol revealed that these are promising materials for the production of biodiesel.^{12–20} Shu et al.²¹ reported the use of inexpensive vegetable oil asphalt for the preparation of a sulfonated carbon-based catalyst useful for the

biodiesel synthesis. Bio-oil, produced from biomass via fast pyrolysis also can be further processed for the production of fuels and chemicals. Bio-char, a by-product from this process has proven to be a promising raw material for the production of activated carbons because of its availability at a low price¹⁹. All these studies indicate the importance and scope in using various types of low value carbon sources for the production of catalytically active carbon materials. Petroleum waste coal tar is another cheaper source material for this purpose as it is easily available and suitable for further treatments with acid for obtaining functionalized carbon material for catalytic applications. This way, the utilization of low cost fossil source provides an economic and environment friendly process for high quality material production.

The present study is aimed to explore the possible conversion of petroleum waste into functionalized active carbon material. The key factor in achieving high acid-bearing porous carbon material lies in balancing the extent of carbonization and sulfonation reactions. Generally, these materials are synthesized in two step procedure involving carbonization of the carbon source followed by its acid functionalization.^{3–6} The two-stage method has the drawback of obtaining highly carbonized material with less active centres required for acid functionalization and less porosity. Since, acidity and porosity are the two important functions essential for the catalytic activity, the applications of such materials exhibited limitations in the studied reactions. Hence, the challenge lies in the synthesis of functionalized carbon materials is to create high density of acid sites along with porosity, especially in the range of nano pores.

Herein we report a simple one-step method for the synthesis of a high acid bearing, nano porous carbon (NPC) nano material facilitated by the simultaneous carbonization and sulfonation of petroleum waste. The new class of this carbon material possessing hydrophobic carbon moiety with hydrophilic $-\text{SO}_3\text{H}$, $-\text{OH}$ and $-\text{COOH}$ groups with its high acidity and nano porous properties, is not only suitable for further functionalization with acid or metal ions but also expected to provide good mechanical and thermal stability for catalytic applications. The material exhibited superior catalytic performance in the bulky molecular transformation of tertiary butylation of phenol in terms of higher conversion, higher selectivity to 2-,4-TBP and stability in the studied period of 4 reaction cycles. The catalytic activity observed here is highest ever reported in the liquid phase reaction over functionalized carbon materials.

Herein we used petroleum waste coal tar as a cheaper and green carbon precursor alternative to the commonly used high cost resins, ionic surfactants and P123 block co-polymers.¹⁰ 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,^{11,12} herein we adopted the simultaneous carbonization and sulfonation method in a single

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[†]Electronic supplementary information (ESI) available: Experimental details, XRD, EDX etc.

step. The synthesis procedure is very simple that involves drop by drop addition of sulphuric acid (55 gm) to 10 gm of coal tar obtained from petroleum waste followed by its treatment at 100 °C for 24 h and then carbonization of the resultant mixture in nitrogen atmosphere at 300 °C to facilitate the decomposition and transformation of the petroleum waste to hydrophobic carbon residue bearing sulfonyl groups. The catalyst material was left for 4 hours in boiling water followed by washing with cold water to remove the weakly bound acid sites and carbon before using as a catalyst.

The wide angle XRD pattern (Fig. 1 ESI) of the sample shows the ordered amorphous nature of the material. The morphology and internal structure of the material analysed by SEM, TEM and HRTEM images (Fig. 1) indicates the formation of porous carbon matrix consists of interconnected nano particles of about 10 nm. The HRTEM image of the material shows the nano porous structure of the carbon with uniform pore size. The porous nature of the material is further supported by N₂ adsorption-desorption isotherm (Fig 2A). The BJH pore size distribution of the sample clearly shows that the major contributions of pores are between 1.7 to 2.6 nm (Fig 2B). The IR spectra of the sample (Fig. 3A) shows broad band centred around 3400 cm⁻¹ representing the OH stretching along with peaks around 2929 cm⁻¹ and 2860 cm⁻¹ related to C–H stretching vibrations. The other band appeared around 1715 cm⁻¹ is due to C=O stretching and that of 1606 cm⁻¹ is related to -OH bending. The peaks related to -SO₃H stretching and O=S=O stretching are appeared at 1207 cm⁻¹ and 1040 cm⁻¹ respectively. Overall, the FTIR spectra indicate the presence of -COOH, -OH, -SO₃H and -CH groups in the material. The elemental analysis and EDX analysis of the material further confirms the presence of carbon, oxygen and sulphur (ESI table 1). The origin of phenolic -OH and -COOH groups can be attributed to the open-air synthesis procedure adopted during the simultaneous carbonization and sulfonation of the material.

The acidity of the functionalized material determined by acid-base titration method (Table 1, ESI) indicates significantly high acid loading occurred on the material (as high as 4.03 mmol/g) by the sulfonation method adopted in the present study. The composition analysis of the material described above indicates the contribution of three functional groups responsible for this acidity, namely, -SO₃H, -COOH and -OH. Among these, the -SO₃H is observed to contribute 1.43 mmol/g of acidity (determined by CHNS and EDX analysis). Rest of the acidity (2.6 mmol/g) can be ascribed to the combined contribution of -COOH and -OH groups. Overall, the presence of -SO₃H, -COOH and phenolic -OH groups in the material are observed to be responsible for the creation of significantly high acidity in the carbon material. Further, the hydrophilic nature of these functional groups on the material is also expected to contribute to the chemical interaction with the hydrophilic reactant molecules to facilitate the reaction in an effective manner.^{22,23} The tertiary butylation of phenol reaction involving hydrophilic reactants has been studied in the present work as it is expected to be encouraged by the hydrophilic acid functional groups present on the acid functionalized carbon moiety.

The thermal stability of the material was determined by TGA analysis (Fig. 3B) which shows the initial weight loss at three places; 1) about 7 % weight loss at 190 °C 2) about 3 % weight loss between 190-282 °C and 3) major weight loss of 30 % at above 282 °C that can be ascribed to the removal of water/moisture, weakly stable carbon moiety and carbon material respectively. The high moisture and water content possessed by the material can be ascribed to the presence of various hydrophilic groups. The TGA/DT analysis indicates that the material is stable up to 282 °C and is suitable for catalytic applications.

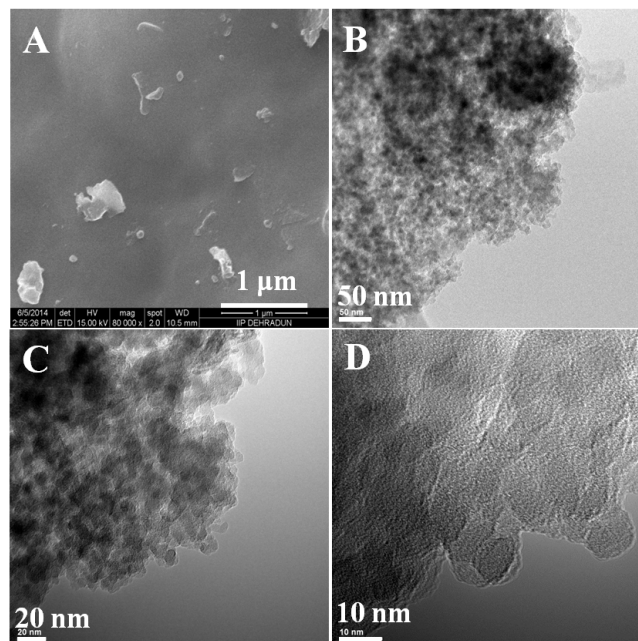


Fig. 1 A) SEM, B & C) TEM and D: HRTEM images of material.

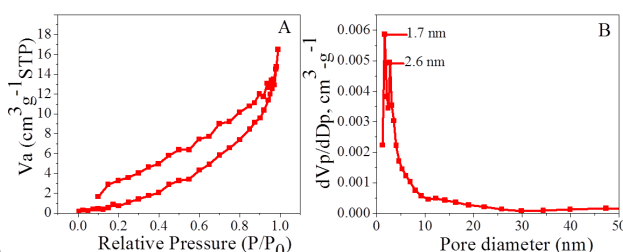


Figure 2 A) N₂ adsorption-desorption isotherms and B) The BJH pore size distribution of the material

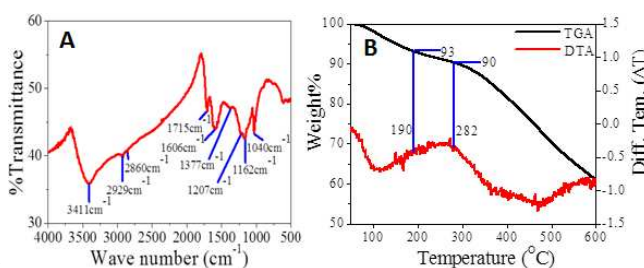


Fig. 3 A) FTIR and B) DT/TGA spectra of the material

The alkylated phenols are very good antioxidants and important raw materials in polymer industry. In general, the tertiary butylation of phenol is conventionally carried out in vapour phase reaction at higher reaction temperatures (above 140 °C) (Table 2 ESI†). However, the recent developments in novel materials giving opportunity for low temperature liquid phase catalytic reactions.²⁴⁻²⁶ The material synthesized in the present study exhibiting strong acidity is expected to be suitable for catalytic applications involving alkylation reaction and the material is tested for its performance in liquid phase butylation of phenol. We have applied the synthesized material for solvent free liquid phase reaction in Parr reactor at 130 °C for 5 h. The studies indeed indicated the promising catalytic functionality of the synthesized material,

Table 1 Catalytic performance of the NPC material^a

SN	RT (h)	Conversion of phenol (wt%)	Selectivity to alkylation products (wt%)			
			2-TBP	4-TBP	2,4-DTBP	Unidentified
1	5	85.0	14.5	14.0	64.4	7.1
2	5	84.0	17.0	13.5	62.0	7.5
3	5	84.5	16.0	14.5	63.0	6.5
4	5	83.0	15.0	14.0	65.0	6.0

^aCatalyst: 0.5 g (5 wt. % of Phenol+TBA), Reaction temperature: 130 °C, pressure: 1 bar N₂; reaction time: 5 h; Phenol/ TBA = 1 : 2.5 (molar ratio).

where, the catalyst exhibited as high as 85% conversion based on phenol (>97% conversion based on alcohol) with product selectivity of 64.5%, 14.5% and 14% to 2,4-ditertiary butyl phenol (2,4-DTBP), 4-tertiary butyl phenol (4-TBP) and 2-tertiary butyl phenol (2-TBP) respectively (Table 1). The results indicate higher conversion, higher selectivity to bulky 2, 4-DTBP product and better performance in terms of low temperature operation and reaction times of the present catalyst when compared to the reported results (Table 2&3 ESI†). The higher performance of the catalyst observed in the present study can be ascribed to the high acid density of the nano porous carbon material obtained in the single step carbonization and functionalization adopted during the synthesis. The present material also exhibited much higher catalytic activity when compared to the –SO₃H containing supports reported in the literature (Table 2&3 ESI). This may be due to the co-presence of the hydrophilic –COOH and phenolic –OH groups in the material of the present study that is expected to play an important role in promoting the effective interaction between hydrophilic reactants and the active sites of the catalyst. Thus the presence of acidic SO₃H groups along with hydrophilic groups (–COOH & –OH) present in hydrophobic carbon of present study provides a beneficial factor for the development of the catalytic process for alkylation reactions, and the catalyst also exhibits constant phenol conversion up to the 4 reaction cycles (Table 1). The reusability of the catalyst synthesized in this work was investigated by filtering the reaction solution, washing the spent catalyst with ethanol and drying at 120 °C between consecutive reaction cycles.

In conclusion, we have demonstrated a facile and single step synthesis method for the preparation of high acidic nano porous carbon material through simultaneous carbonization and sulfonation of petroleum waste. The method is cheaper and produces thermally stable material suitable for catalytic applications involving bulky organic transformations. Here we have achieved as high as 4.03 mm/g acidity responsible for as high as 85% phenol conversion in the alkylation reaction. The porous nature of the material also reflected in the production of high amount of bulky 2,4-DTBP (65%). The phenol conversion and the selectivity towards 2,4-DTBP on the present catalyst system are observed to be highest ever reported on the

functionalized carbon materials to the best of our knowledge. Moreover, the active material does not suffer from leaching problems and can be efficiently reused in consecutive catalytic cycles.

We acknowledge the CSIR for the research funding of the project under 12th FYP. Authors are thankful to the director, IIP, for his encouragement. DN thankful to CSIR, New Delhi, for awarding senior research fellowship and Deepak Rohilla for helping in reaction studies. We are thankful to XRD, IR and SEM, groups at IIP for analysis.

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