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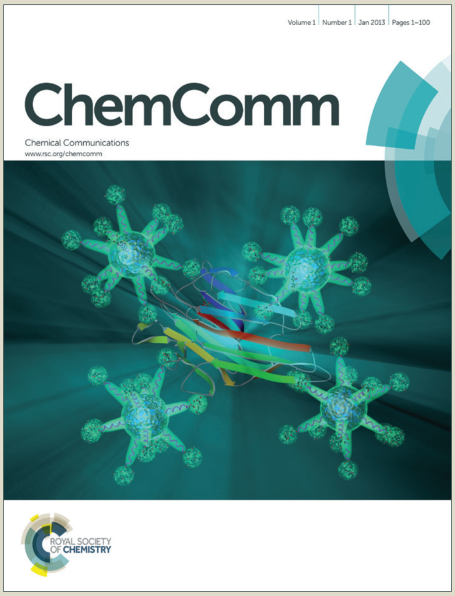

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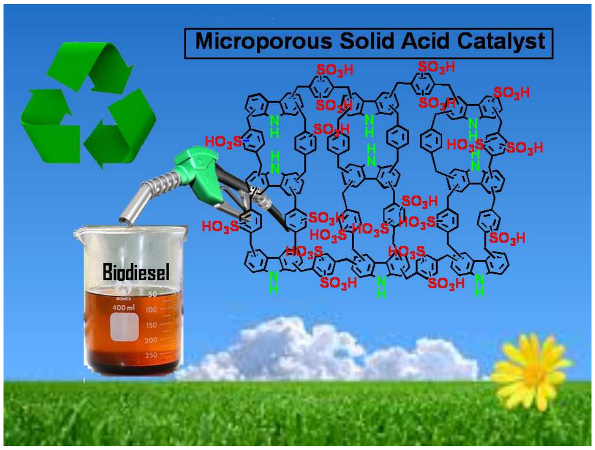
Graphical Abstract

A new hypercrosslinked supermicroporous polymer, scope for sulfonation and its catalytic potential for the efficient synthesis of biodiesel at room temperature

Subhajit Bhunia, Biplab Banerjee and Asim Bhaumik*



A new supermicroporous polymer with BET surface area of 913 m^2g^{-1} have been synthesized via Friedel-Crafts alkylation between carbazole and α,α’-dibromo-*p*-xylene and upon sulfonation it yielded a very efficient solid acid catalyst for the production of biodiesels at room temperature.

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We have designed a new hypercrosslinked supermicroporous polymer (HMP-1) having BET surface area of 913 m^2g^{-1} by $FeCl_3$ catalyzed Friedel-Crafts alkylation reaction between carbazole and α,α′-Dibromo-*p*-xylene and upon sulfonation HMP-1 yielded a very efficient solid acid catalyst for the production of biodiesels via esterification/*trans*-esterification of free fatty acids (FFA) /esters room temperature.

Functionalized porous organic materials are very demanding, owing to their huge potential in many application areas like adsorption, supercapacitors, gas storage and catalysis.[1] Microporous polymers with pore diameters <2 nm, high BET surface area and bearing basic N-sites at their surfaces are particularly demanding for the adsorption of large amount of green house gas CO_2.[2] A wide range of microporous materials, like zeolites[3], metal-organic frameworks (MOFs),[4] zeolitic imidazole frameworks (ZIFs)[5] and porous organic polymers (POPs)[6] have been invented. These materials have found versatile uses in many application areas of energy and environmental research. Numerous ranges of microporous organic polymers can be designed by direct polymerization of rigid building blocks through condensation, coupling and cyclization reactions.[7] Being abundant in nature and inexpensive, carbon-based precursors are attracting larger interests for materials design and utility. Further, from the perspective of green synthesis, carbon-based catalysts have immense potential as the sustainable alternatives over existing MOFs, zeolite, metal oxides and metal-grafted heterogeneous catalysts. In this context it is worthy to mention that standard biodiesel production involves the catalytic transesterification of long or branched chain triglycerides with short-chain alcohols.[8] Conventional catalysts are strong acids or strong bases like mineral acids or metal hydroxides, which are homogeneous in nature and thus associated with problems in separation and purification. Thus, more active, eco friendly, green heterogeneous catalysts for the production of biodiesels are very demanding. Heterogeneous catalysts based on zeolites,[9] metal oxides, metal phosphonates,[10] MOFs and completely carbonized organic materials are often employed for these reactions. But the synthetic methodologies are complicated and often involve lengthy multistep organic syntheses, specialized starting materials or need of inert reaction conditions. Microporous polymers have been employed for a wide range of catalytic reactions in recent times.[11] Zeolite,[12] metal oxide, metal organic framework based solid acid catalysts for bio-fuel production have the main drawback of significant metal leaching in the reaction medium.[13] From that point of view high surface area metal-free acidic carbocatalysts are much more advantageous than metal based acidic catalysts.[14] Synthesis of solid acid carbocatalysts often involves incomplete carbonization, high reaction temperature together with complicated methodology. So considering all the drawbacks of the organic, inorganic and organic-inorganic hybrid materials, herein we first report a less expensive, scalable, efficient metal-free acidic solid carbocatalyst HMP-1 by the Friedel-Crafts alkylation between carbazole and α,α′-dibromo-*p*-xylene over the Lewis acid catalyst anhydrous $FeCl_3$, followed by the post synthetic modification of HMP-1 via sulfonation to obtain HMP-1-SO_3H (Fig. 1).

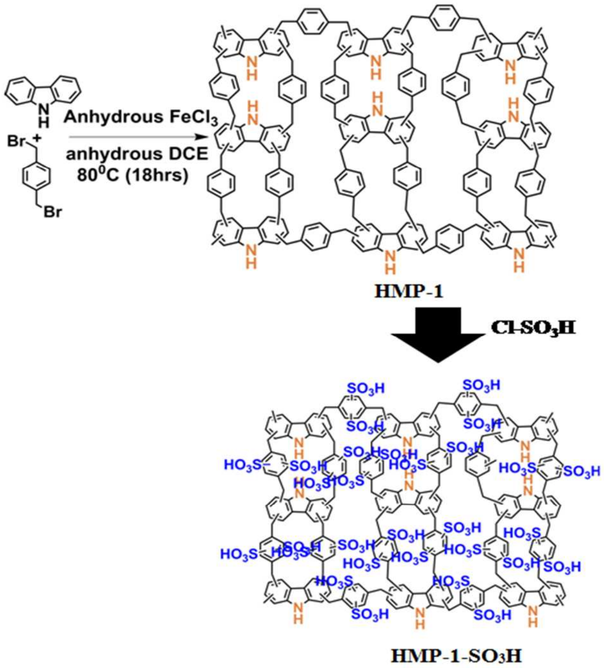


Figure 1. Friedel Crafts alkylation reaction between carbazole and α,α′-Dibromo-*p*-xylene followed by sulfonation to obtain HMP-1-SO_3H.

The synthesis of hypercrosslinked polymer HMP-1 had been carried out in dichloroethane solvent. The FTIR spectrum of HMP-1 (ESI Figure S1a,c) shows no peak corresponding to the C-Br bond, also confirmed by colorimetric NBP test.[15] Peak at 2900 cm^{-1} corresponding to phenylic C-H bond and peak at 3400 cm^{-1} for the N-H stretching of carbazole is clearly seen. The peaks at 1022 cm^{-1} and 1039 cm^{-1} are the evidence of additional crosslinking during sulfonation.[15] However, HMP-1 is completely amorphous in nature as revealed from the powder XRD data (ESI Fig. S2). α,α′-dibromo-*p*-xylene is used as linker here because it bears the unsubstituted carbon atoms of benzene rings for post synthetic functionalization. N_2 adsorption/desorption isotherms of HMP-1 and HMP-1-SO_3H are shown in Fig. 2a. These isotherms are mostly type I in nature suggesting the presence of intrinsic framework microporosity in the material. The BET specific surface area of HMP-1 is 913 m^2g^{-1}. After sulfonation the BET surface area is considerably decreased to 346 m^2g^{-1}, although the isotherm retains type I nature.

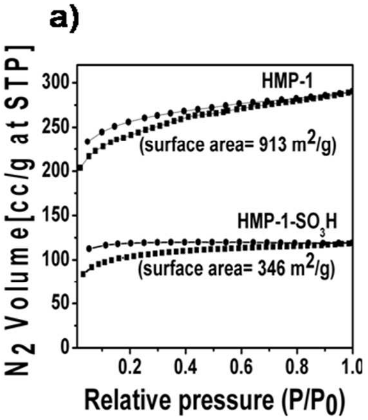


Figure 2 (a) N_2 adsorption/desorption isotherms of HMP-1 and HMP-1-SO_3H. Adsorption points are marked by filled square and desorption points by filled circle b) pore sized distribution of HMP-1 by NDLFT method c) pore size distribution of HMP-1-SO_3H by NDLFT method.

The pore size distribution of HMP-1 and HMP-1-SO_3H using carbon cylindrical pore model of non local density functional theory (NLDFT) at 77 K (Figure 2b,c) suggested the peak pore size distribution at 1.6 nm for the former, which on sulfonation decreased to 1.54 nm. This result suggested grafting of a large amount of sulfonic acid group in the aromatic moieties of the organic framework. Solid state ^{13}C MAS NMR study gives the useful information about the chemical environment of different Carbon atoms present in HMP-1 and HMP-1-SO_3H. The peak at 37.7 ppm is for the methylene carbon ([a]). The peaks at 111.8 ppm and 156.9 ppm are assigned for the carbons [f] and [e] of the carbazole moiety (ESI† S1b). Two intense peaks at 129.2 and 139 ppm could be assigned to the arometic tertiary[c,d,j,g] and quaternary carbons[b,i,k][16] of the HMP-1 network. The downfield chemical shifts of the 13C signals of the benzylic and benzenoid carbons together with peak broadening observed for HMP-1-SO_3H (ESI† S1d) suggested the random sulfonation of the benzene rings. HRTEM image of HMP-1 material has been shown in Fig. 3. It is clear that HMP-1 possesses inter-grown spherical morphology which are uniformly distributed throughout the specimen grid. The scanning electron microscopic (SEM) images of HMP-1 reveal that the particles are spherical in shape and their size is varying from 50 to 200 nm, which is in close agreement with TEM image analysis. No morphological change has been observed after sulfonation (ESIFig. S3). TGA-DTA plot suggested that HMP-1-SO_3H is less stable than HMP-1 due to desulfonation at 150-200 ^0C (ESI Fig. S4). Temperature programmed desorption of NH_3 (NH_3-TPD) was carried out to measure the total acidity of HMP-1-SO_3H. The NH_3-TPD result is shown in (ESI Fig. S5). In the TPD profile two humps are observed. The low temperature hump is smaller than the higher temperature one. The area under first hump corresponding to 353.7 K gives the amount of ammonia chemically desorbed. This corresponds to the total amount of acidic sites present in the catalyst. Observed big hump beyond 473 K is not considered as this peak could be associated with the decomposition of organic framework at high temperature. The total acidity of this HMP-1-SO_3H catalyst is 3.7 $mmolg^{-1}$. This result matches well with acid-base titration result (ESI: Sec. S2). We had synthesized HMP-1 several times varying the molar ratio of two monomers and sulfonated them to obtain HMP-1-SO_3H with optimized acidity (ESI, Fig S6).

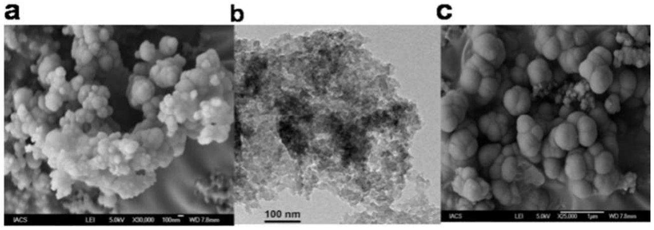


Figure 3 SEM images of HMP-1 at different magnification (a,c). b)TEM image of HMP-1

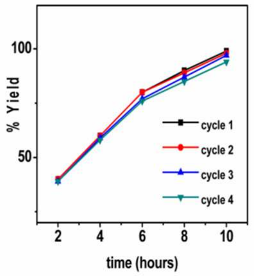
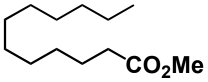
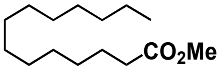
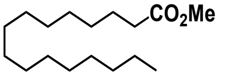
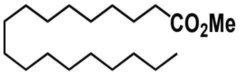
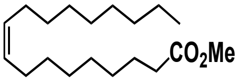
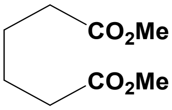
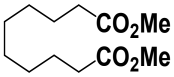
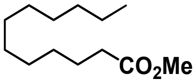
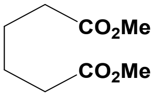


Figure 4 Recyclibility of HMP-1-SO_3H carbocatalyst in the esterification of lauric acid

The catalytic activity had been tested in the esterification of long chain free fatty acids with methanol at room temperature. The reaction time was *ca.* 10-12 h for various substrates. In this reaction methanol plays the role of both solvent and reagent. Solid acid catalysts for the esterification of FFA are very much desirable for successful and economical synthesis of biodiesels. Several solid acid catalysts have been reported so far for the production of biodiesels. When the esterification of lauric acid was performed over HMP-1-SO_3H at 298 K for 10 h the yield of FAME became *ca.* 99%. We had carried out esterification reactions taking seven different long chain fatty acids with methanol (Table 1). As seen from the Table 1 that for all long chain fatty acids the yield of biodiesel products ranged between 93-99%. After completion of the reaction, the reaction mixture was filtered to remove the catalyst and then methanol was evaporated. The yields of esterification reactions were measured by taking the weight of dried products and they were characterized by ^1H and ^{13}C NMR analysis (ESI Fig. S7-S21). In a typical catalytic reaction 0.5 mmol of long chain fatty acid was dissolved in 2 ml methanol and 6 mg catalyst was added and the progress of the reaction was monitored by TLC. It takes 10-12 h to complete the reaction at room temperature. The catalyst was filtered, dried and used for the same reaction for four times to understand the recycling efficiency of HMP-1-SO_3H (Fig. 4). Retention of high catalytic activity for four consecutive cycles suggested very high catalytic efficiency of HMP- 1-SO_3H. As the boiling point of fatty acid ester is much higher than methanol, the product was easily isolated by vacuum evaporation of methanol. We have also performed transesterification of soybean oil with methanol (oil:MeOH=1:100) at room temperature as well as elevated temperature. The efficacy of this catalyst is evaluated quantitatively from the yield (%) of fatty acid methyl ester (FAME) calculated with respect to the glycidic proton as shown in ^1H NMR spectra (ESI: Fig. S22). For soybean oil the yield of FAME at 298 and 333 K for 12 h reactions are 30 and

55%, respectively. The composition of FAME is determined from the GC-MS analysis of the reaction mixture (ESI: Fig S23), suggesting that soybean oil is composed of 16% stearic, 38% *cis*-linoleic, 42% octadecynoic and 4% heptanoic acid.

Table 1. Biofuel synthesis over HMP-1-SO_3H

Fatty acid	Acid:MeOH (mmol)	Time h	Temp. K	Product	Yield[a] (%)
Lauric acid	1:50	10	298		99
Myristic acid	1:50	10	298		99
Palmitic acid	1:50	10	298		98
Stearic acid	1:50	12	**2**98		93
Oleic acid	1:50	12	298		94
Adipic acid	1:100	12	298		95
Sebacic acid	1:100	12	298		97
Lauric acid[b]	1:50	24	323		9
Adipic acid[b]	1:100	24	323		11

[a] Isolated and purified yield using HMP-1-SO_3H as catalyst, ^1H and ^{13}C NMR for all products are given in ESI: Figure S7-S21. [b]HMP-1 is used as catalyst.

Conclusions

We can conclude that a new hypercrosslinked microporous organic polymer HMP-1 can be synthesized via the Friedel-Craft alkylation between carbazole and α,α′-Dibromo-*p*-xylene. HMP-1 upon sulfonation yields a cost effective, highly acidic carbocatalyst HMP 1-SO_3H, which showed excellent catalytic activity for biodiesel production at room temperature. As biodiesel is major alternative to fossil fuel because of the diminishing petroleum stock and HMP-1-SO_3H showed very high yields of the biodiesel products under very mild reactionconditions, sulfonated porous polymer reported herein may find huge potential as a solid acid catalyst in future.

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Notes and references

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Electronic Supplementary Information (ESI) available: Experimental and characterization of the catalyst and ^1H and ^{13}C NMR data are reported here. For details please see DOI: 10.1039/c000000x/

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