Applied Catalysis A: General 513 (2016) 19–29

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Porous carbonaceous solid acids derived from farm animal waste and their use in catalyzing biomass transformation

Iman Noshadi[b,*], Baishali Kanjilal[c], Fujian Liu[a,*]

[a] Department of Chemistry, Shaoxing University, 312000 China
[b] Harvard-MIT Division of Health Sciences & Technology, Massachusetts Institute of Technology (MIT), Cambridge 02139, USA
[c] Institute of Materials Science, University of Connecticut, Storrs, CT 06269, USA

ARTICLE INFO

Article history:
Received 8 September 2015
Received in revised form
21 December 2015
Accepted 22 December 2015
Available online 29 December 2015

Keywords:
Disposal cow manure
Carbonaceous solid acids
Acid catalysis
Biomass transformation
Porous materials

ABSTRACT

We demonstrate here the transformation of waste cow manure into N rich porous carbons (NPC) with large amount of micropores and large Brunauer–Emmett–Teller (BET) surface areas. The transformation process was achieved *via* carbonization of cow manure in presence of $ZnCl_2$ and $FeCl_3$ additives, without using additional templates. The resultant NPC could be converted into microporous carbonaceous solid acids (NPC-[C_4N][X]) by quaternary ammonization of samples with 1,4-butane sultone, and ion exchanging with strong acids such as HSO_3CF_3 and H_2SO_4. X-ray diffraction patterns and Raman spectra showed that NPC-[C_4N][X] exhibit amorphous carbon network. N_2 isotherms and SEM images showed that NPC-[C_4N][X] have abundant nanopores with large BET surface areas. XPS, FT-IR and elemental analysis results showed the N rich network in NPC support, has been successfully and homogeneously functionalized with strongly acidic ionic liquid and sulfonic groups. ^{31}P solid NMR spectra confirmed that NPC-[C_4N][X] have typical Brønsted acid centers with strong and controllable acidity. Catalytic tests showed that NPC-[C_4N][X] exhibits excellent activity and reusability in production of biofuels and fine chemicals through esterifications, transesterifications, and depolymerization of microcrystalline cellulose. This approach may provide a novel and cost effective way to recycle the waste cow manure into efficiently porous carbon based solid acids for heterogeneous acid catalysis.

1. Introduction

Recently, significant efforts have gone into development of solid acids as alternatives to mineral acids to catalyze transformation of low cost feedstocks into useful chemicals and biofuels [1–8]. In comparison to mineral acids, the solid acids catalysts exhibit unique characteristics which include low toxicity, reduced corrosion, environmentally friendly, easy separation from reaction mixtures, good product selectivity and reusability. This underscores their potential importance in the areas of green and sustainable chemistry [3–14]. The general framework of solid acids comprises of versatile compositions based on silicas, metal oxides, polymers and carbons [5,6,15–17]. While inorganic solid acids like zeolites, sulfated metal oxides and sulfonic group functionalized mesoporous silicas show good thermal stabilities, with wide applicability as reusable acid catalysts, their hydrophilic framework results in the deactivation of acidic centers by water, which usually released as a byproduct in many acid-catalyzed reactions [5,6,10,18,19]. Additionally, limited concentrations of active acid sites also leads to a constraint in their catalytic applications [8,15,20–22]. The development of polymeric solid acids with controllable hydrophobicity and wettability basically overcome the disadvantages of the above inorganic solid acids such as deactivation of acidic sites by water and low concentrations of acidic sites [4,8,23,24]. While polymeric solid acids such as macroporous acidic resins and mesoporous polymeric solid acids show excellent catalytic activities and good reusability in esterification, transesterification and condensation reactions, the relatively low thermal stability of polymeric networks imposes constraints on their applications at high reaction temperatures [4,8,23–25].

These limitations can be overcome by employing carbonaceous networks, which possess controllable hydrophobicity, good thermo-mechanical and chemical stabilities [26–30]. Such networks can then serve as supports for grafting with acidic groups. Hara and coworkers synthesized carbonaceous solid acid by heating aromatics such as naphthalene in sulfuric acid at high temperatures up to 473–573 K. The resultant solid acids showed good

* Corresponding authors.
E-mail addresses: inoshadi@mit.edu (I. Noshadi), fjliu1982@gmail.com (F. Liu).

http://dx.doi.org/10.1016/j.apcata.2015.12.032
0926-860X/

catalytic activity in esterification and hydrolysis [31]. To facilitate rapid diffusion of reactants and products in and out of the solid acids, a mesoporous structure is desirable and hence sulfonic group functionalized mesoporous carbons have been systematically studied. Sulfonic group functionalized ordered mesoporous carbons with large BET surface areas and abundant nanopores have been synthesized by Wang et al. [32]. The resultant mesoporous carbon based solid acids were observed to act as highly active protonic acid sites for catalyzing synthesis of Bisphenol-A [32]. In the meantime, other groups have also synthesized various sulfonic groups functionalized ordered mesoporous carbons [33–35], however, the high cost and complex synthetic procedures associated with their preparation largely constrain their widely industrial applications, especially in large scale [32–36].

Thus the key to effective application of carbonaceous solid acids lies in reducing their cost of production and environmental pollution. Low cost biomass such sugars and crystalline cellulose could be used as raw materials for preparation of carbonaceous solid acids [16,17,37], wherein the solid acids comprise of flexible polycyclic aromatic carbon nanosheets with SO_3H, COOH and phenolic OH groups in a 3D network [16,17,37]. Alternative biomass resources such as corn straw, microalgae residue, bagasse and vegetable oil asphalt could also be used as precursors for synthesizing carbonaceous solid acids [38–41]. However, till date, there have been few reports on transformation of waste and low cost feedstocks, which need fiscal investment for their disposal, into carbonaceous solid acids. We report here the synthesis of highly porous and efficient carbonaceous solid acids (NPC-[C_4N][X]) derived from waste cow manure for the first time, a very low cost feedstock. The waste cow manure was firstly transformed into N rich nanoporous carbons (NPC) *via* carbonization in the presence of $ZnCl_2$ and $FeCl_3$ additives without using any other templates. This was followed by treatment with 1,4-butane sultone and ion exchange with strong acids such as HSO_3CF_3 and H_2SO_4. Notably, the resultant NPC-[C_4N][X] showed excellent activity and good reusability in the reactions of esterification of fatty acid with methanol, transesterifications of oil with methanol, and depolymerization of microcrystalline cellulose into fine chemicals, which was much better than those of commercially acidic resin of Amberlyst 15, H-ZSM-5, reported carbonaceous solid acids and sulfonic group functionalized ordered mesoporous silica (SBA-15-SO_3H). This work provides a cheap alternative precursor to the manufacture of carbonaceous solid acid structures, which puts forth a new idea in the synthesis of efficient porous carbonaceous solid acids from very low cost waste cow manure, with a potential for widespread catalytic applications to synthesis of various chemicals in industry.

2. Experimental sections

2.1. Chemicals and reagents

All reagents were of analytical grade and used directly without further purification. $FeCl_3$, $ZnCl_2$, tripalmitin, Amberlyst 15, Amberlyst 70, toluene, CH_2Cl_2, 1,4-butane sultone, trifluoromethanesulfonic acid, sulfuric acid, oleic acid, methanol, poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide) (Pluronic P123, molecular weight of about 5800), 3-mercaptopropyltrimethoxysilane (3-MPTS), tetraethyl orthosilicate (TEOS), microcrystalline cellulose, gamma valerolactone (GVL) and $H_3PW_{12}O_{40}$ were purchased from Sigma–Aldrich Company, Ltd (USA). H-form zeolite was supplied by Sinopec Catalyst Co. Brown grease oil was extracted from the wastewater treatment plant, which was obtained from Torrington city in Connecticut. The resultant brown grease contains 89% of FFA and 11% of tri, mono and di glyceride. The waste cow manure was obtained from grassland.

2.2. Preparation of catalysts

2.2.1. Synthesis of NPC

Before carbonization, the waste cow manure [H_2O (~10.4 wt%), total fiber (~52.6 wt%), lignin (~13 wt%), cellulose (~12.2 wt%), hemicellulose (~27.4 wt%), proteins (~18.1 wt%), total nitrogen (~2.62 wt%), phosphorous (~0.51 wt%), sulphur (~0.31 wt%) and other compositions] was washed with hexane for 3 times, dried under vacuum condition for 3 days, and then became powder by using grinder. In a typical synthesis of NPC, 3 g of dry cow manure without further treatment was mixed with 9 g of $ZnCl_2$ in 50 mL of 3 M $FeCl_3$ solution at a temperature of 80 °C. The slurry was stirred at 80 °C for 3 h, till most of the water was evaporated. The remaining mass was dried at 100 °C to constant weight in a hot air oven whereby the carbon precursor was obtained. Subsequently, the activation and carbonization process of the carbon precursor was carried out in a tubular furnace under a N_2 atmosphere by heating the sample at a rate of 5 °C/min up to 900 °C for 1 h. To purify the NPC, the carbonized sample was washed with abundant hydrochloric acid to removing metal species, and the residual hydrochloric acid could be removed from washing of the sample with large amount of water until neutral. Finally, NPC was dried at 60 °C under vacuum condition, which showed the yield at around 40% with the concentrations of C, N, O, P, Cl and S at around 61.4, 2.52, 6.4, 1.3, 2.2 and 0.32 wt% respectively.

2.2.2. Synthesis of strong acid ionic liquids functional NPC of NPC-[C_4N][SO_3CF_3].

NPC-[C_4N][SO_3CF_3] was synthesized from quaternary ammonization of NPC with 1,4-butane sultone, followed by an anion

Table 1
The textural and acidic parameters of various catalysts.

Samples	Acid contents (mmol/g)[a]	*N* content (mmol/g)[b]	S_{BET} (m^2/g)[c]	V_p (cm^3/g)[c]	D_p (nm)[d]
NPC	–	1.80	2434	1.52	1.8
NPC-[C_4N][SO_3CF_3]	1.25	1.76	726	1.31	1.8
NPC-[C_4N][SO_3CF_3][e]	1.21	1.71	706	1.28	1.6
NPC-[C_4N][SO_4H]	1.22	1.72	701	1.29	2.1
SBA-15-SO_3H	1.98	–	814	1.4	7.5
$H_3PW_{12}O_{40}$	3.5	–	4.8	–	–
Amberlyst 15	4.7	–	45	0.31	40
[C_4vim][SO_3CF_3]	2.96	–	–	–	–
H_2SO_4	10.2	–	–	–	–

[a] The acid concentration was obtained from acid-base titration.
[b] The data was obtained from CHNS elemental analysis.
[c] The data was obtained from N_2 adsorption.
[d] The pore diameters were calculated from BJH model.
[e] Recycled NPC-[C_4N][SO_3CF_3] in catalyzing microcrystalline cellulose transformation.