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Graphical Abstract

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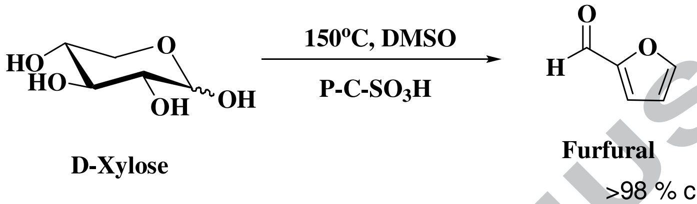

>98 % conv
>99 % selectivity

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Sulfonated polymer impregnated carbon composite as a solid acid catalyst for the selective synthesis of furfural from xylose

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ABSTRACT

A sulfonated polymer impregnated carbon composite solid acid catalyst was prepared by the pyrolysis of a polymer matrix impregnated with glucose followed by its sulfonation and used for the dehydration of xylose to furfural. The developed catalyst exhibited excellent activity and provided almost quantitative conversion of xylose with the selective synthesis of furfural. After completion of the reaction, the catalyst was easily recovered and reused for several runs without noticeable loss in its activity and selectivity.

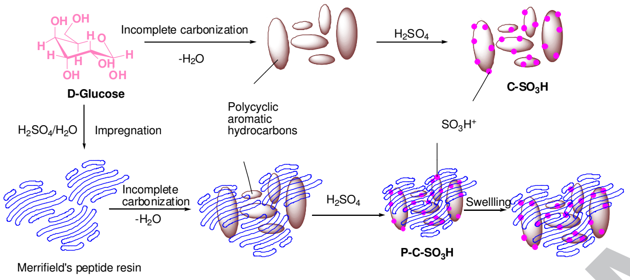
Conversion of biomass through green chemical routes is of great industrial importance as biomass is considered to be most widely available inexpensive renewable resource that can be used as a raw material for the production of biofuel and value-added organic products. In this regard, acid catalyzed dehydration of biomass derived pentose sugars (mainly D-xylose) to furfural is a process of tremendous research interest in current scenario due to the wider industrial applications of furfural.[2] Furfural is an excellent organic solvent for refinement of lubricants and separation of butadiene from butene mixture in synthetic rubber fabrication. In addition it also serve as a promising solvent for many organic materials, such as resins, polymers and also used as a building block for synthesis of various valuable chemicals such as furfuryl alcohol, furan, pharmaceutical, agrochemicals and THF.[3-5]

The conventional approach for dehydration of xylose to furfural involves the use of highly corrosive and toxic acids such as concentrated sulfuric acid, hydrochloric acid etc as catalyst and higher reaction temperatures.[6-7] Under these conditions, the selectivity of furfural does not exceed 70 %, unless is continuously extracted with supercritical fluids. Furthermore, the process can also promote a number of secondary reactions which affects the overall selectivity of the desired product. Subsequently a number of efforts have been made to develop cost effective, environmentally benign and selective catalytic processes for the conversion of xylose to furfural. In this regard, different solid acid catalysts including zeolites[8-11], heteropolyacids[12] and sulfonic acid functionalized mesoporous/microporous materials,[13-17] transition metal oxides and titanates,[18-20] MCM-41-supported niobium-oxide,[21] ion exchange polymer resins like Nafion and amberlyst,[22-24] vanadyl pyrophosphate[25] have been reported for this transformation. The merits of solid acid catalysts lie in their higher activity, selectivity, and ease of separation from the reaction products. Furthermore, they are considered as super acids due to the higher acid strength which is possibly similar to or greater than the acidity exhibited by strong mineral acids, such as concentrated sulfuric acid. However, most of the existing catalytic systems suffer from the drawbacks such as high activation barrier for xylose dehydration, high reaction temperature, longer residence period in aqueous media and limited recyclability. Recently, Yu and coworkers[26] reported the synthesis of magnetic porous carbonaceous solid acid catalyst derived from biomass waste for the dehydration of xylose to furfural with excellent conversion. However poor selectivity and longer reaction time (5h) limited the scope of this investigation. In another report Luong et al demonstrated the applicability of graphene, graphene oxide, sulfonated graphene, sulfonated graphene oxide as solid acid catalyst for dehydration of xylose to furfural in aqueous media but it is associated with high operating temperature and relatively lower yield, making the process unfavorable.[27]

Recently low cost sulfonated carbon catalysts ($C–SO_3H$) derived from the incomplete carbonization of simple sugars such as glucose has come out to be a new class of catalysts exhibiting superior activities than several sulfonated acid catalysts, for example silica supported Nafion, sulfonated zirconia etc for acid catalyzed reactions.[28-29] However, added stability is another appealing aspect of sulfonated carbon materials in addition to low cost. In this regard, Goodwin et al[30] reported sulfonated carbon composite solid acid prepared by the pyrolysis of a polymer matrix impregnated with glucose followed by sulfonation as catalyst for the biodiesel synthesis. The title catalyst exhibited higher acid site density, better esterification activity of both small and large free fatty acids (acetic acid and palmitic acid), and superior reusability than the previously reported carbon-based catalyst prepared by sulfonating pyrolyzed sugar. Inspired with these results, we thought it would be worthwhile to explore the potential of such catalysts in the area of biomass conversion to value added chemicals. Accordingly, herein we report an efficient sulfonated polymer impregnated carbon composite solid acid catalyst for the dehydration of xylose to furfural selectively in good to excellent yield under comparatively milder reaction conditions.

Synthesis and characterization of the catalyst

During the present study, the targeted sulfonated polymer impregnated carbon composite (P–C–SO_3H) was synthesized via sulfonation of a composite material formed through incomplete carbonization of hydrolyzed glucose supported in a polymer matrix based on a copolymer of styrene and chloromethylstyrene i.e. Merrifield resin (Scheme 1).[31] For the comparative study, the corresponding sulfonated carbon catalyst (C-SO_3H) was also synthesized via incomplete carbonization of glucose.[32]



Scheme 1: Synthesis of P-C-SO_3H and C-SO_3H catalysts

The powder X-ray diffraction of the synthesized P-C-SO_3H catalyst did not show any characteristic peak and exhibited a broad peak centered at 2θ value of 25°, indicating that the synthesized material is amorphous in nature (Fig. S1), which is in well conformity with the existing literature report.[30]

FT-IR spectra of the synthesized P-C-SO_3H and C-SO_3H catalysts are shown in Fig. S2. As shown, the broad absorption band around 3300 cm^{-1} in P-C-SO_3H was attributed to OH stretching with two shoulder peaks due to aromatic C-H stretching and aliphatic C-H stretching. Double headed absorption band in the region 1630–1780 cm^{-1} was related to the C=O group. Much stronger absorption bands around 1000 cm^{-1} and 630 cm^{-1} in P-C-SO_3H compare to C-SO_3H are assigned to S=O stretching of -SO_3H and C-S stretching respectively which clearly suggested the higher loading of the acid sites in the polymer impregnated carbon catalyst i.e. P-C-SO_3H than C-SO_3H. The poor acidity of carbon (C-SO_3H) catalyst was further proved by a very weak band around at 1200 cm^{-1} due to the asymmetric and symmetric stretching of sulfonic acid group, which is quite stronger in P-C-SO_3H.

Sulfur contents or sulfonic acid site densities in both P-C-SO_3H and C-SO_3H catalysts were estimated by elemental analysis (Table 1). The acidity of the P-C-SO_3H and C-SO_3H calculated from elemental sulfur analysis assuming that all the sulfur atoms in the catalyst are presented in -SO_3H form was found to be 2.44 and 1.28 mmol H^+/g, respectively. This is most likely due to the freely distribution of polycyclic aromatic hydrocarbons along to the resin framework are much more even which lead to the greater availability of active sites for sulfonation, resulted in the higher sulfonic acid density of P-C-SO_3H as compared to the of C-SO_3H.[30]

Table 1: Properties of the sulfonated catalysts

Catalyst	BET surface area (m2/g)	SO_3H(mmol/g) by elemental S analysis
P-C-SO_3H	<1 (<1)*	2.44 (2.42)*
C-SO_3H	<1(<1)*	1.28 (0.66)*

*values in parenthesis are of composites of ref. 30

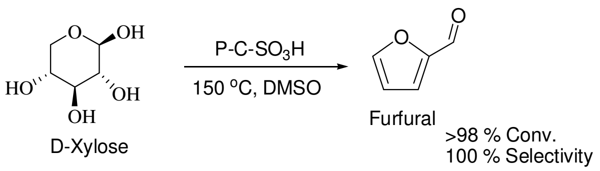
The surface properties and acid densities of the synthesized composite P-C-SO_3H were found to be comparable with the existing literature.[30] However the synthesized C-SO_3H displayed almost twofold excess acid density as compared to the value reported by Goodwin etal.[30]

Thermal stability of the synthesized carbon-based catalysts was determined by thermal gravimetric analysis (TGA). The both catalysts showed almost similar decomposition pattern when heated in air (Fig. S3). An initial weight loss was due to water desorption as the temperature increased from room temperature to 100 °C. Furthermore in the temperature range of 150–500 °C, the TGA pattern of P–C–SO_3H showed a plateau indicating a much slower rate of weight loss than C-SO_3H. Finally a rapid weight loss was occurred in the temperature range 550 to 650 °C when negligible mass was left at this temperature.

Catalytic activity

The catalytic activity of the synthesized catalysts P-C-SO_3H and C-SO_3H was checked for the dehydration of xylose to furfural at 150 °C using DMSO as reaction media.[33] Among the two catalysts studied sulfonated polymer impregnated carbon composite (P-C-SO_3H) was found to be superior and provided almost quantitative conversion of xylose with the selective synthesis of furfural (Table 2, entry 1-2). Based on these results we have chosen P-C-SO_3H as catalyst for further study and performed a number of experiments in order to identify the optimized reaction conditions. The results of these experiments are summarized in Table 2. At first, the dehydration of xylose to furfural was performed in water at 150 °C for 30 min (Table 2, entry 3). The reaction was found to be very slow and gave extremely poor conversion of xylose to furfural (>1%). However, the reaction was found to be increased with time and gave only marginally improved yield after 3h (Table 2, entry 3-6). Consequently, a biphasic solvent system such as mixture of water and toluene (1:3, v/v) was used at 150 °C for 2 h (Table 2, entry 7). The reaction did not occur and unreacted xylose was recovered at the end of the reaction. Next, the reaction was carried out using water/ DMSO in different ratios under otherwise similar reaction conditions (Table 2, entry 8-9). The reaction was found to be slow and gave maximum 45 % conversion of xylose to furfural in 2 h when 1:5 ratio of water and DMSO was used as reaction media (Table 2, entry 9). Inspired by these findings next we tried the reaction in DMSO at 150 °C. Surprisingly the reaction was found to occur at faster rate and gave nearly 72 % conversion of xylose with 98 % selectivity for furfural in 1h (Table 2, entry 10). Based on these experimental results we have chosen DMSO as the solvent of choice for further studies. Further we studied the effect of reaction time by keeping other reaction parameters constant. As expected the conversion of xylose was found to be increased with time and gave 92 % conversion in 2h (Table 2, entry 11) and almost quantitative conversion (> 98 %) within 3h (Table 2, entry 1). Temperature was also found to be a key factor in this reaction and gave best results at 150 °C. Further increase in temperature did not show any appreciable improvement in the results (Table 2, entry 12-13).

Table 2: Dehydration of xylose to furfural under different reaction conditions[a]



Entry	Solvent	Time/ h	Temp/ °C	Conv. (%)[b]	Selec (%)[b]
1	DMSO	3.0	150	98	100
2[c]	DMSO	3.0	150	45	98
3	H_2O	0.5	150	1	95
4	H_2O	1.0	150	1	99
5	H_2O	2.0	150	1.5	94
6	H_2O	3.0	150	2.5	92
7	H_2O/Toluene (1:3)	2.0	150	-	-
8	H_2O/DMSO (1:3)	2.0	150	24	96
9	H_2O/DMSO (1:5)	2.0	150	45	95
10	DMSO	1.0	150	72	97
11	DMSO	2.0	150	92	99.2
12	DMSO	3.0	120	12	96
13	DMSO	3.0	160	45	97.5

[a]Reaction conditions: xylose (0.5 g, 3.33 mmol), solvent (25 ml), catalyst (0.1 g.), [b]conversion and selectivity were determined by HPLC; [c]C-SO_3H was used as catalyst.

The greater catalytic activity of P-C-SO_3H as compared to C-SO_3H can be explained on the basis of a flexible polymeric framework decorated along with a layer of sulfonated polycyclic aromatic hydrocarbons, which can quickly swell the liquid phase enabling the reactant xylose to access more active sites as compared to in C-SO_3H catalyst. Furthermore, structure directing property of polymer matrix or resin is also an additional factor for the higher stability of P-C-SO_3H through interaction between carbon moieties and the polymer framework.

Last but not the least, recycling ability of the developed P-C-SO_3H was tested by performing a number of recycling experiments under similar experimental conditions. After completion of the reaction, the catalyst was recovered by simple filtration and reused for the dehydration of xylose to furfural under optimized reaction conditions. The recycling ability of the catalyst was tested for six subsequent runs (Fig. 1). In these experiments the conversion of xylose to furfural was as good as with first run of catalyst. Furthermore, the sulfur content of the recovered catalyst obtained after six runs was found to be almost similar to the fresh one. These results established that the synthesized composite catalyst is highly stable and can be efficiently recycle for several runs.

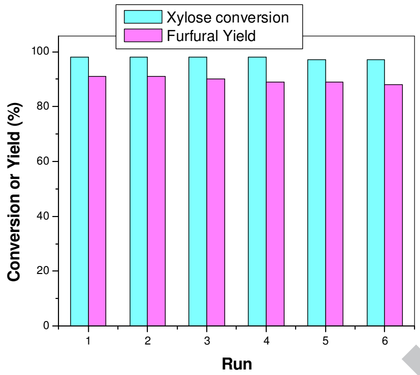


Fig. 1: Results of recycling experiments;

In summary, we have demonstrated sulfonated polymer impregnated carbon composite (P-C-SO_3H) as an efficient and selective solid acid catalyst for the dehydration of xylose to furfural. The sulfonated polymer impregnated carbon composite i.e. P-C-SO_3H was found to be superior than sulfonated carbon catalyst (C-SO_3H) and afforded almost quantitative conversion of xylose with the selective synthesis of furfural. The higher catalytic activity of P-C-SO_3H may be due to the more even distribution of polycyclic aromatic moieties along the resin network, leading to more available sites for sulfonation which resulted in greater sulfonic acid density in P-C-SO_3H as compared to in C-SO_3H. After completion of the reaction, the catalyst was easily recovered and reused subsequently for several runs without significant loss in its activity.

Calculations

The organic phase samples were first subjected to GC-MS analysis to establish the compounds extracted from the reaction medium; no major products or intermediates other than furfural were detected. Furfural in the organic phase samples was quantified via HPLC using C18 column with water (0.05 mmol H_2SO_4) as mobile phase at a flow rate of 0.6 mL min^{-1} and the column temperature was maintained at 333 K and detector temperature of 35 °C were used for optimal peak resolution and detection. Furfural in the organic phase samples was quantified via HPLC analysis. Xylose conversion, furfural selectivity and furfural yield were calculated as given below.

$$Conversion = \frac{\text{mol of initial xylose} - \text{mo. of unreacted xylose}}{\text{mol of initial xylose}}$$

$$Selectivity = \frac{\text{mol of furfural produced}}{\text{mol of initial xylose} - \text{mol of unreacted xylose}}$$

$$Furfural\ yield = \frac{\text{Furfural yield obtained}}{\text{Furfural yield theoritical}} \times 100$$

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31. *Preparation of the polymer impregnated-SO_3H functionalized carbon composite (P-C-SO_3H):* In a typical experiment, a solution of glucose (2.0 g) in 3 ml of deionized water was added with 2 drops of sulfuric acid (H_2SO_4) and the resulting mixture was slowly added to a pre dried Merrifield peptide resin (2 g) with magnetic stirring. After complete addition of glucose solution, the resulting mixture was dried at 110-120^{o}C for 12 h. Thus obtained black material was crushed to powder and then pyrolyzed under dry nitrogen at 300^{o}C for 1h in a muffle furnace. The resulting black residue was subjected to sulfonation by using concentrated sulfuric acid (1g. solid/ 20 ml H_2SO_4) at 160^{o}C for 12 h under nitrogen atmosphere. The mixture was diluted with plenty of distilled water and the black material so obtained was collected by filtration, washed several times with hot distilled water of 80^{o}C until impurities like sulfate ions were no longer detected in the wash water. The resulting black solid (P-C-SO_3H) was dried in an oven at 80^{o}C under vacuum for 5 h.
32. For the comparative studies, a sulfonated carbon catalyst (C-SO_3H) was synthesized by the heating of D-glucose powder (10 g.) at 400^{o}C for 15 h under dry N_2 atmosphere by incomplete carbonization. The resulting black material was crushed to powder and then subjected to sulfonation with conc. H_2SO_4.
33. *General Procedure for dehydration of xylose to furfural*: dehydration of xylose to furfural was carried out in a 100 cc stainless steel parr reactor. In a typical batch experiment a solution of xylose (0.5 g), DMSO (25 ml) and catalyst (0.1g) were charged into the reactor. The reactor vessel was sealed and heated at 150 ^{o}C for desired reaction time. After completion of desired run time, reactor was cooled down to room temperature. Catalyst was filtered off by simple filtration and washed several times with acetone and dried in oven at 70^{o}C to use subsequently for next cycle. The conversion of xylose and selectivity for the furfural was analyzed by HPLC using C18 column with water (0.05 mmol H_2SO_4) as mobile phase at a flow rate of 0.6 mL min^{-1} and the column temperature was maintained at 333 K. HPLC chromatogram of the product is given in the supporting information (Fig. S4). Furthermore, the product was confirmed by ^{1}H NMR analysis (Supporting Fig. S5).

Supplementary Material

Characterization of the catalyst is given in the Supplementary information file.