



Original Research Paper

Novel synthesis of Lewis and Bronsted acid sites incorporated CS-Fe₃O₄@SO₃H catalyst and its application in one-pot synthesis of tri(furyl)methane under aqueous media

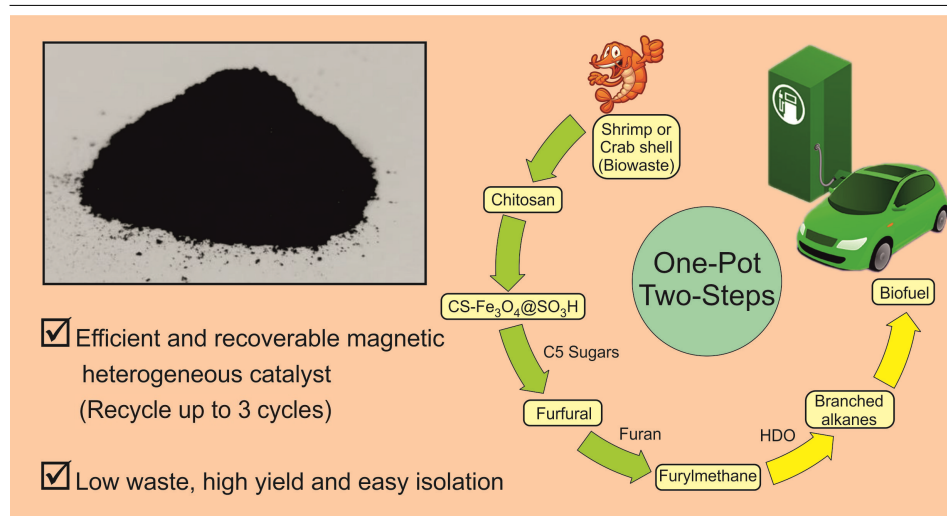
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HIGHLIGHTS

- Efficient synthesis of novel chitosan-based carbonaceous catalyst by one step low-temperature carbonization/sulfonation.
- The catalyst showed excellent selectivity for the conversion of C5 sugars into furfural followed by tri(furyl)methane.
- One-pot two-step dehydration/condensation reactions with efficient yields.

GRAPHICAL ABSTRACT



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ABSTRACT

A sustainable chitosan (CS)-derived magnetic solid acid catalyst (CS-Fe₃O₄@SO₃H) incorporated by Lewis and Bronsted acid sites was synthesized in an eco-friendly manner through the preloading of iron on CS and one-pot low-temperature carbonization/sulfonation. The carbonization/sulfonation of CS-Fe₃O₄ using *p*-Toluenesulfonic acid (*p*-TSA) at 140 °C resulted in the loss of ammonia in some extent and provided bifunctional sites on the catalyst. This heterogeneous catalyst was found to be highly selective for the conversion of xylose and arabinose to furfural (FF) and subsequent tri(furyl)methane (TFM) formation by the condensation with furan in the same reaction vessel without any purification. The outcome of optimization under different reaction parameters showed that only 20 wt.% of CS-Fe₃O₄@SO₃H catalyst resulted in 81% TFM yield from xylose while arabinose gave a 70% TFM yield in dimethyl sulfoxide (DMSO):water with high selectivity. This green protocol provides an easy isolation of products and minimizes the formation of polymerized by-products. The catalyst can be readily recovered and efficiently reused for three consecutive catalytic cycles without any significant loss on product yields.

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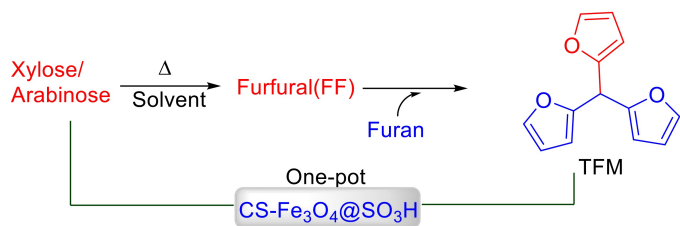
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1. Introduction

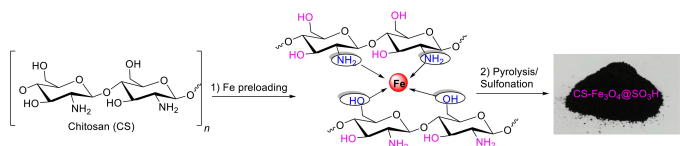
Biomass is an abundant carbon-containing resource in nature. It can be converted into various value-added compounds and advanced liquid fuels, providing alternative material/energy sources in the biosphere (Chatterjee et al., 2015; Wang et al., 2015; Lin et al., 2017). There exist serious concerns regarding the continuously increasing global population and the subsequent impacts on fossil fuels consumption. Hence, there is a need to look for alternative energy sources. In addition, sustainable and renewable substitutes to traditional fossil resources are highly essential to tighten the gap between the supply and demand of feedstock used for fuels and chemicals production (Huber et al., 2005; Xing et al., 2010). Tri(furyl)methane (TFM) is among the most versatile and promising compound derived from biomass and has gained a great deal of attention because of its wide range of industrial applications (Butin et al., 1999). It is an important intermediate for the synthesis of tetraoxaquerene (Pejewski et al., 2004), agrochemicals (Nakanishi et al., 1969), polymers (Hall, 1984; Gandini and Salon, 1990), macromolecules for use as metal ion carriers (Musau and Whiting, 1994), etc. Moreover, TFM derivatives could also be used as carbon source for the synthesis of branched alkanes through hydroxydeoxygenation (HDO) (Huang et al., 2012; Yang et al., 2013; Balakrishnan et al., 2014a).

Owing to its importance and usefulness, many researchers have synthesized TFM directly from commercially available furfural (FF). Usually, the furyl methane derivatives are synthesized from FF and furans through condensation by several homogeneous and heterogeneous catalysts such as HCl (Balakrishnan et al., 2014a), conc. H_2SO_4 (Corma et al., 2011), $AuCl_3$ (Nair et al., 2005), MCM- SO_3H (Van Rhijn et al., 1998), zeolites (Algarra et al., 1995), SiO_2 -Pr-S-Pr- SO_3H (Balakrishnan et al., 2014b), CMH- SO_3H (Ogino et al., 2015), SILC (Li et al., 2015), and TFA-ZrO₂ (Zhu et al., 2016). However, several disadvantages associated with these catalysts like activity loss, long reaction time, catalyst separation, and high cost are still challenging and should be overcome. Hence, there is a need to design mild, robust, more economically-viable, and environmentally-benign heterogeneous catalysts for the synthesis of TFM directly from pentose (C5) sugars.

Heterogeneous solid acid catalysts in general play a vital role in the transformation of biomass and its derivatives to fuels and value-added chemicals (Toda et al., 2005; Yan et al., 2009; Alonso et al., 2010; Haung et al., 2013; Thombal and Jadhav, 2016a; Tiwari et al., 2017). Among those, sulfonated carbonaceous catalysts are basically more fascinating due to their good thermal stability, high acid strength, and reusability. Herein, we report on the synthesis of a novel, green, and recyclable carbonaceous solid acid catalyst ($CS-Fe_3O_4@SO_3H$) and investigated its application for innovative one-pot synthesis of TFM from C5 sugars (Schemes 1 and 2). To the best of our knowledge, the fabricated catalyst and the one-pot synthesis of TFM from C5 sugars have not been studied previously.



Scheme 1. One-pot reaction design for the synthesis of TFM from xylose and arabinose over $CS-Fe_3O_4@SO_3H$.



Scheme 2. Synthesis of sulfonated magnetic $CS-Fe_3O_4@SO_3H$ carbonaceous solid acid catalyst.

2. Materials and Methods

2.1. Materials

CS, ferric chloride, and *p*-Toluenesulfonic acid (*p*-TSA) were obtained from Sigma-Aldrich (USA). Xylose and arabinose were bought from Alfa Aesar (USA) and aqueous ammonia solution was obtained from Duksan Pure Chemicals (South Korea). All the solvents were obtained from Sigma-Aldrich (USA). All purchased chemicals and solvents were used without further purification.

2.2. Catalyst preparation and characterization

$FeCl_3$ solution with a 100 mmol.L⁻¹ concentration was added into a suspension of CS (80% deacetylated) (3 g) in 100 mL water with continuous stirring in a round-bottomed flask. The solution was stirred for 5 h at room temperature. An aqueous solution of ammonia was added drop wise into the solution to maintain the pH around 9-10. Then, the mixture was simply filtered and the solid residue was dried at 300 K overnight. The resulting powder ($CS-Fe_3O_4$) was then heated with *p*-TSA in an oil bath at 140 °C for 24 h under a nitrogen atmosphere (Thombal and Jadhav, 2016b). After 24 h, the catalyst was kept open to air and further heated for 24 h to remove all the volatile compounds adsorbed on the surface of the material. Subsequently, the mixture was cooled to room temperature. The resulting solution was then filtered and washed thoroughly with deionized water to remove excess of sulfate ions and finally with absolute ethanol to remove all the water. The black solid obtained was dried in an oven at 300 °K for 24 h. The obtained black powder was named as $CS-Fe_3O_4@SO_3H$ catalyst.

The catalyst obtained was characterized by Fourier transform infrared spectroscopy (FT-IR, Perkin-Elmer Spectrum Two™ IR Spectrometer), X-ray diffraction (XRD, Panalytical X'Pert pro MPD), field emission scanning electron microscopy (FE-SEM, Hitachi S4200) equipped with an energy dispersive X-ray micro-analysis (EDAX) detector, X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha System), field emission transition electron microscopy (FE-TEM, FEI Tecnai F20), and acid-base titration.

2.3. General procedure for the synthesis of TFM

In a typical synthesis, xylose/arabinose (1 mmol) and $CS-Fe_3O_4@SO_3H$ (20 wt.%) catalyst were taken in a round-bottomed flask under air atmosphere, to which 6 mL of solvent was added. The reaction was then heated at 140 °C for 24 h under magnetic stirring. Then, the reaction mass was cooled to room temperature and furan (8 eq) was added. Subsequently, reaction stirring was continued at room temperature for 10 h (xylose) and 8 h (arabinose). At the end of the reaction, the solid catalyst was magnetically separated from the reaction mixture and the reaction mass was extracted with ethyl acetate (25 mL × 3). The solvents were evaporated under reduced pressure and the residue was purified using column chromatography (EtOAc/Hexanes). The formation of FF and TFM was confirmed by their NMR analysis and by comparison with the reports available in the literature (Bhaumik and Dhepe, 2014; Shinde and Rode, 2017).

3. Results and Discussion

3.1. Properties of $CS-Fe_3O_4@SO_3H$ catalyst

The FT-IR spectra of CS, $CS-Fe_3O_4$, and $CS-Fe_3O_4@SO_3H$ are shown in Figure 1a. The bands observed in the range of 3296-3355 cm⁻¹ in the spectra of CS, $CS-Fe_3O_4$, and $CS-Fe_3O_4@SO_3H$ were assigned to the O-H asymmetric stretching and N-H stretching vibrations. The weak band appeared at 2876 cm⁻¹ could be assigned to the aliphatic stretching vibrations of C-H of the -CH₂ groups in CS. This peak appeared with a very low intensity in $CS-Fe_3O_4@SO_3H$ catalyst was due to the residual carbon matter after low temperature pyrolysis. The peak observed for all the three materials at 1628 cm⁻¹ could be associated with the stretching of C=O of HN=C=O bonds (Mohseni-Bandpi et al., 2015). The signal at 1592 cm⁻¹ was ascribed to the bending of NH₂ group of CS while the peaks around 1370 cm⁻¹ indicated the C-N stretching vibration. The stretching of C-O

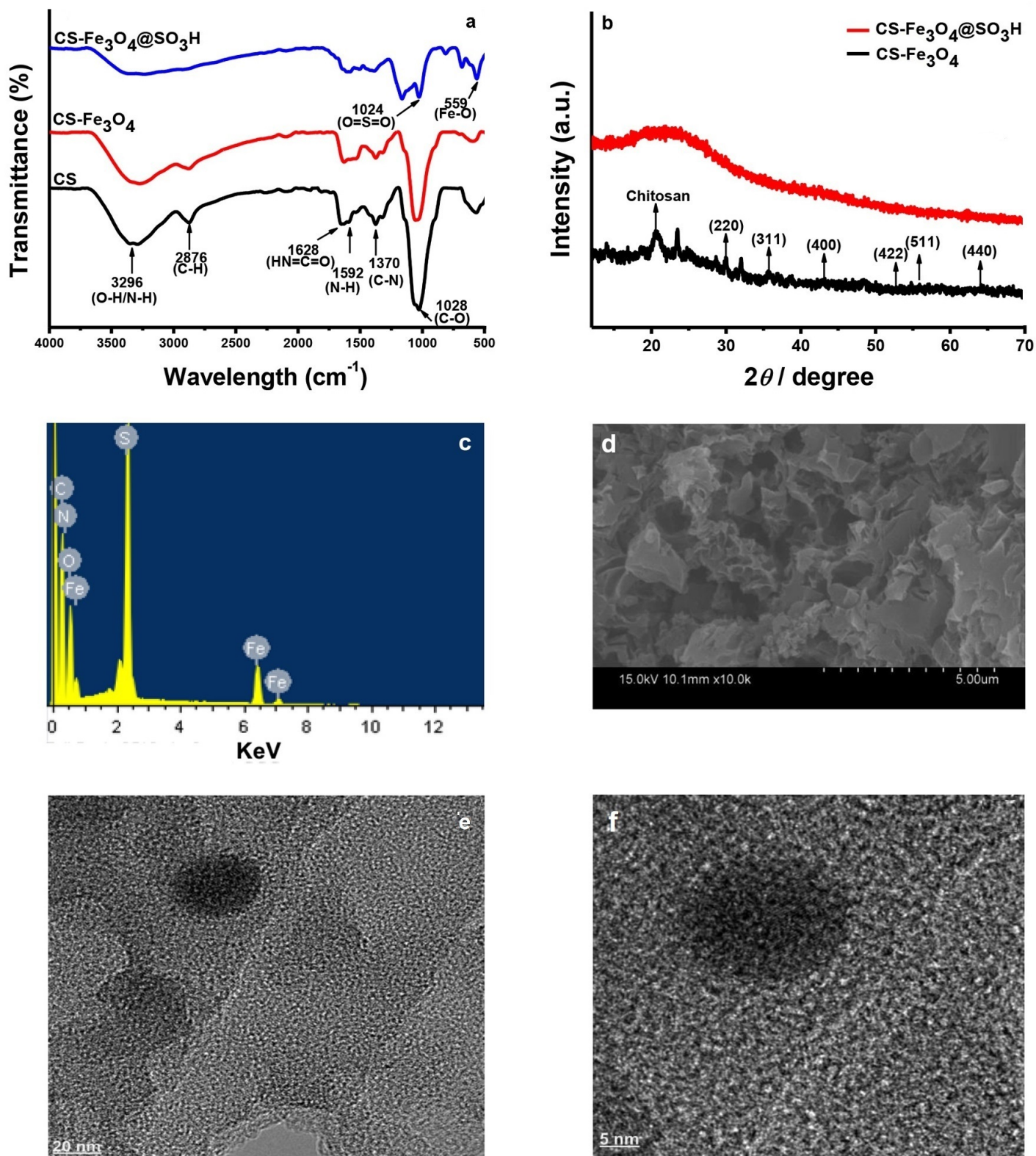


Fig. 1. (a) FTIR spectra of CS, CS-Fe₃O₄, and CS-Fe₃O₄@SO₃H catalyst; (b) XRD patterns of the CS-Fe₃O₄ and CS-Fe₃O₄@SO₃H; (c) EDAX spectra of CS-Fe₃O₄@SO₃H; (d) SEM image of CS-Fe₃O₄@SO₃H; and (e and f) TEM images of CS-Fe₃O₄@SO₃H.

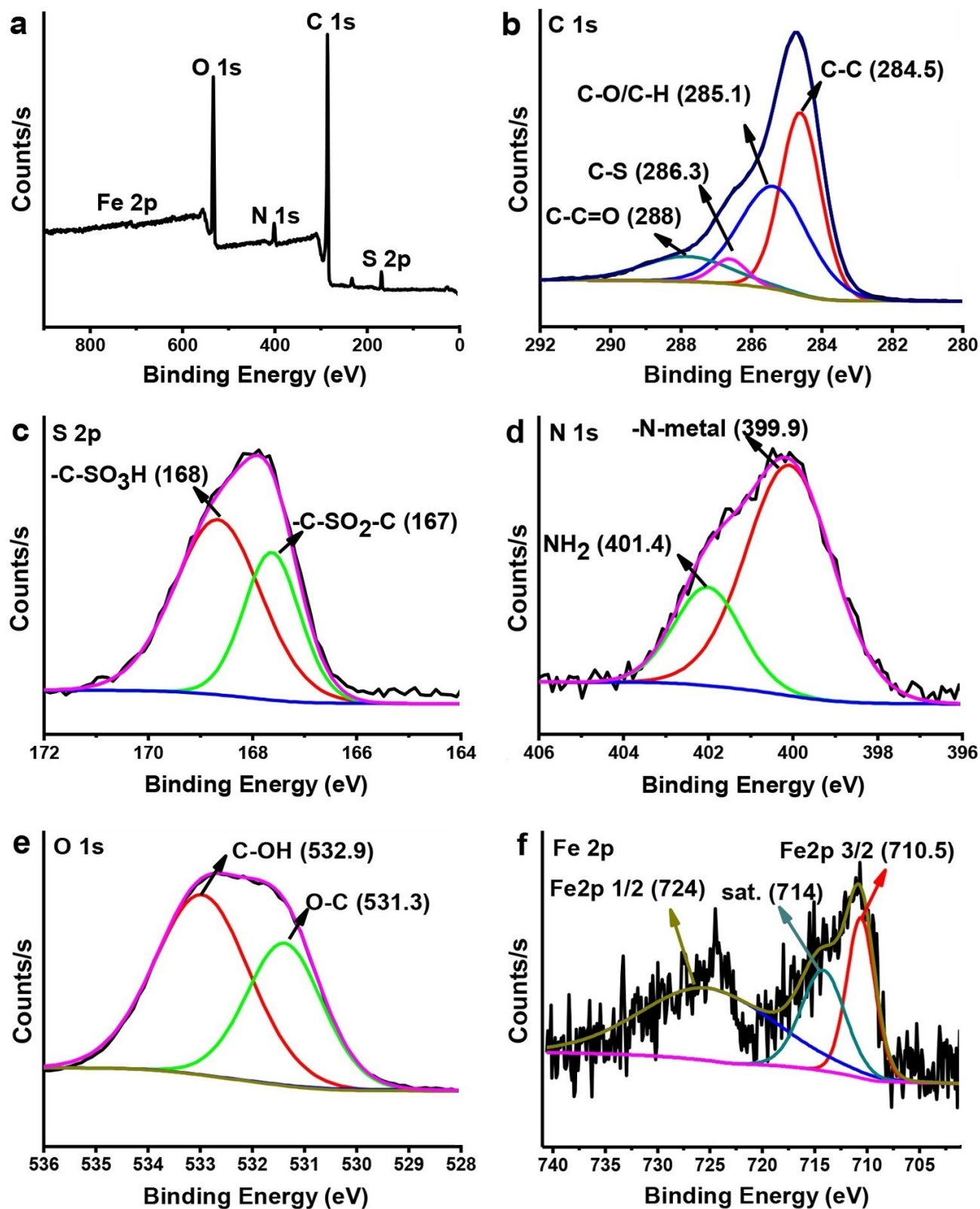


Fig. 2. (a) XPS survey scan spectrum of CS-Fe₃O₄@SO₃H. (b-f) deconvoluted XPS spectra of C 1s, S 2p, N 1s, O 1s, and Fe 2p, respectively.

bond resulted in a band at 1028 cm^{-1} . The peak at 602 cm^{-1} was obtained due to saccharide structure of CS. The bonds around 559-580 cm^{-1} were observed in the spectra of the CS- Fe_3O_4 and CS- Fe_3O_4 @ SO_3H , which could correspond to the Fe-O band vibration of Fe_3O_4 . The CS- Fe_3O_4 @ SO_3H catalyst spectrum revealed a peak at 1024.3 cm^{-1} which could be attributed to the O=S=O asymmetric and symmetric stretching vibrations of - SO_3H groups (Thombal and Jadhav, 2016b). Hence, the FT-IR spectra clearly confirmed the presence of Fe and sulfonated groups on the surface of CS- Fe_3O_4 @ SO_3H catalyst. The XRD patterns of CS- Fe_3O_4 and CS- Fe_3O_4 @ SO_3H catalyst are shown in Figure 1b. The XRD pattern of CS- Fe_3O_4 indicated six main peaks at $2\theta = 30.0^\circ$, 35.4° , 43.0° , 53.3° , 56.9° , and 62.5° corresponding to the indices (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1), and (4 4 0), respectively. These confirmed the crystalline nature of CS- Fe_3O_4 (Zulfikar et al., 2016). Along with these, a very weak and broad band was observed at 2θ angles of 12° - 18° , which was related to the amorphous CS polymer. However, the CS- Fe_3O_4 @ SO_3H catalyst showed a broad diffraction peak over the 2θ range of 15 to 30° , which could typically be attributed to the amorphous carbon composed of aromatic carbon sheets considerably oriented in a random fashion. Thus, the XRD patterns confirmed the amorphous nature of the synthesized catalyst. The EDAX analysis revealed that the surface of the catalyst was mainly composed of C, O, N, Fe, and S. The atomic percentages of S and Fe were found to be 7.59 and 3.79%, respectively (Fig. 1c). The composition of N was found to be negligible probably due to the loss of ammonia during the synthesis of the catalyst. The SEM image of the catalyst clearly indicated the formation of porous carbonaceous sheets (Fig. 1d). The TEM images of the CS- Fe_3O_4 @ SO_3H at different magnifications exhibited the presence of randomly arranged carbon sheets with Fe ions (Figs. 1e and f). XPS analysis showed the surface composition of the CS- Fe_3O_4 @ SO_3H , confirming the presence of carbon, sulphur, nitrogen, oxygen, and iron in the catalyst (Fig. 2a). The high-resolution C 1s spectrum showed four main deconvoluted peaks at the binding energies of 284.5, 285.1, 286.3, and 288.5 eV which were attributed to the C-C, C-O/C-H, C-S, and C=O, respectively. The S 2p spectrum showed two main peaks at 167.6 and 168.6 eV which corresponded to the -C-SO₂-C- and -C-SO₃H, respectively. The two major peaks in N 1s spectra were observed at 399.9, and 401.4 eV corresponding to the N-metal and unreacted -NH₂ groups, respectively. The O 1s spectra showed two main peaks at 531.3 and 532.9 eV which confirmed oxygen bound to organic compounds and C-OH bonds, respectively. The binding energy values for Fe 2p spectrum included three deconvoluted peaks, i.e., Fe 2p_{3/2} (710.5 eV), Fe 2p_{1/2} (724.3 eV), and another weak satellite peak at 714.2 eV (Figs. 2b-f). The total acid densities and the sulfonic acid densities of CS- Fe_3O_4 @ SO_3H were calculated by acid-base titration and found to be 4.1 mmol g⁻¹ and 2.3 mmol g⁻¹, respectively (See Sup, Table S1) (Suganuma et al., 2008; Thombal et al., 2015).

3.2. Optimization of the reaction conditions for formation of FF from xylose and arabinose

Initially, the activity of CS- Fe_3O_4 @ SO_3H catalyst was studied for the synthesis of FF from xylose and arabinose in various green solvent systems so as to obtain higher yields and the results are summarized in Table 1. First, the reaction was carried out in water at 140 °C using 10 wt.% catalyst for 24 h (Table 1, entry 1) but it led to very low yield of product because water was not favourable for dehydration reactions. Various organic solvents were then screened along with water. When the reaction was carried out in H₂O/Toluene (2:1, v/v) as a solvent system under the given reaction conditions (Table 1, entry 2), FF was produced at a lower yield. Moreover, by replacing toluene with 1-butanol in water, the xylose conversion was extremely decreased and only 11% FF yield was obtained (Table 1, entry 3). Subsequently, a H₂O/Tetrahydrofuran (THF) solvent system was used and the yield of FF was increased to 32% (Table 1, entry 4). Afterwards, the conversion of xylose was carried out in various solvent systems such as H₂O/2-Methyl THF, H₂O/Acetonitrile (CH₃CN), H₂O/ γ -Valerolactone (GVL), H₂O/Nitromethane, H₂O/N-Methyl-2-pyrrolidone (NMP), and H₂O/Dimethyl sulfoxide (DMSO) (Table 1, entries 5-10). Surprisingly, the reaction proceeded at a good rate in the H₂O/DMSO solvent system and the yield of FF was recorded at about 72%. Having obtained a favourable yield using the H₂O/DMSO solvent system, we then tried the reaction in pure DMSO solvent (Table 1, entry 11). However, the conversion of xylose led to a moderate FF yield (51%). Considering the outcomes of these experiments, H₂O/DMSO was selected as an ideal solvent system for further studies.

Catalyst loading was further studied and it was found that FF formation with 20 wt.% catalyst stood at as high as 84% (Table 1, entry 12). Correspondingly, when the reaction time was increased to 48 h, the FF yield was slightly decreased (Table 1, entry 13). By changing the solvent system ratio to 1:1 (v/v), the FF yield was recorded at 63% (Table 1, entry 14). With increasing or decreasing the temperature (i.e., at 120 °C and 160 °C), we observed that the FF yields obtained were slightly decreased (Table 1, entries 15 and 16). In the absence of catalyst, the reaction did not proceed even after 24 h (Table 1, entry 17). On the other hand, a good isolated yield of FF (76%) was obtained from arabinose under H₂O/DMSO solvent system (2:1, v/v) at 140 °C (Table 1, entry 18). In general, water along with non-polar solvents did not generate favourable FF yields, while polar solvents such as 2-Methyl THF, GVL, Nitromethane, and NMP led to promising FF yields due to the highly polar nature of the C5 sugars and their solubility.

Table 1.
The activity of CS- Fe_3O_4 @ SO_3H catalyst for the synthesis of FF from xylose and arabinose using various green solvent systems.^a

Entry	Sugar	Solvent	Catalyst (wt.%)	Temp (°C)	Yield (%) ^b
1 ^c	Xylose	H ₂ O	10	140	8
2	Xylose	H ₂ O/Toluene	10	140	21
3	Xylose	H ₂ O/1-butanol	10	140	11
4	Xylose	H ₂ O/THF	10	140	32
5	Xylose	H ₂ O/2-Methyl THF	10	140	58
6	Xylose	H ₂ O/CH ₃ CN	10	140	16
7	Xylose	H ₂ O/GVL	10	140	63
8	Xylose	H ₂ O/Nitromethane	10	140	42
9	Xylose	H ₂ O/NMP	10	140	52
10	Xylose	H ₂ O/DMSO	10	140	72
11 ^c	Xylose	DMSO	10	140	51
12	Xylose	H ₂ O/DMSO	20	140	84
13 ^d	Xylose	H ₂ O/DMSO	20	140	78
14 ^e	Xylose	H ₂ O/DMSO	20	140	63
15	Xylose	H ₂ O/DMSO	20	120	60
16	Xylose	H ₂ O/DMSO	20	160	63
17	Xylose	H ₂ O/DMSO	-	140	0
18	Arabinose	H ₂ O/DMSO	20	140	76

^a) Experimental conditions for all the entries unless stated otherwise (C5-sugar (1 mmol), solvent system (2:1) 6 mL, CS- Fe_3O_4 @ SO_3H (wt.%), 24h, in a screw capped vial). ^b) Isolated yields. ^c) Solvent 6 mL. ^d) Reaction performed for 48 h. ^e) Solvent system (1:1) 6 mL.

3.3. Impacts of reaction time and furan equivalents in one-pot approach on TFM formation

After evaluating the optimum conditions for FF formation from xylose and arabinose, we further tried to investigate TFM formation in the one-pot system at different time intervals and furan equivalents. For this reaction, the FF mass obtained from xylose and arabinose was cooled down to room temperature and furan (6 eq) was added to the crude mixture. To study the effect of time, six different sets of the experiments were performed at different time intervals. In the case of xylose, the reaction reached the maximum TFM formation within 10 h with 70% yield with 5% of FF recovery. While in the case of arabinose, maximum TFM was obtained within 8 h with 67% yield. These results showed that the conversion of intermediates to the final product, i.e., TFM was greatly dependent on the time or in better words, TFM yield of was increased by increasing reaction time (Figs 3a and b). Subsequently, to look into the effect of furan equivalents on TFM yield, different equivalents of furan were added to the reaction mixture. Based on the results shown in the Supplementary (Figs. S1a and b), the addition of a higher equivalent of furan increased the formation rate of TFM. Interestingly, the addition of 8 eq of furan was

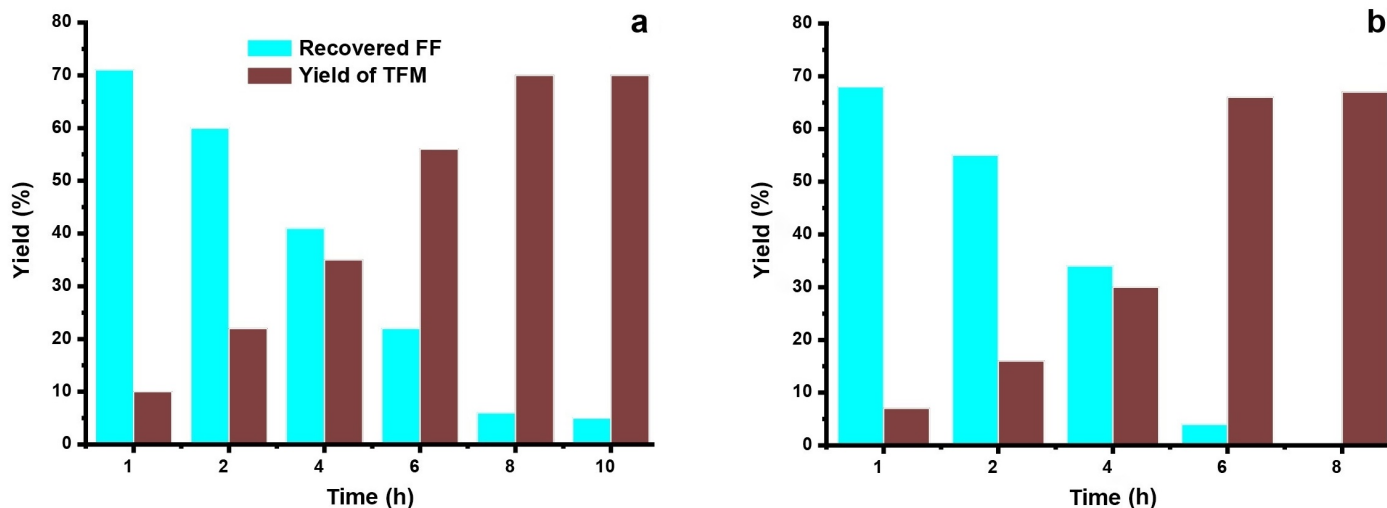
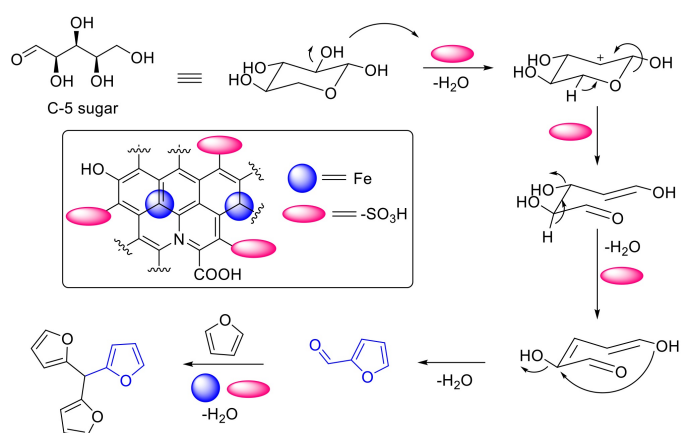


Fig. 3. Impact of reaction time on conversion of (a) xylose and (b) arabinose to TFM.

effective to produce a high amount of product from both xylose (81%) and arabinose (70%).

3.4. Reaction mechanism

The proposed reaction mechanism for the conversion of pentose sugars into TFM catalysed by CS-Fe₃O₄@SO₃H catalyst is suggested in Scheme 3. Accordingly, the process for the formation of TFM from pentose sugars includes several steps like dehydration, ring opening, ring closing, and condensation. Initially, the oxygen atom at C2 is protonated by -SO₃H groups of the catalyst. Then, this results in the loss of water and a carbocation is formed on the ring. To stabilize the cation, electrons from the neighbouring oxygen atom are transferred leading to the simultaneous breakage of the C-O bond and ring opening (Yan et al., 2014). Cyclization followed by elimination of water molecule results in FF production, which through condensation with furan in the presence of iron as well as -SO₃H acid sites successively produce TFM as final product.



Scheme 3. Proposed reaction mechanism for the formation of TFM.

Table 2.

Comparison of the findings of the present study with those of the previous investigations on the conversion of C5 sugars into FF and the subsequent conversion of FF to TFM.

Feedstock	Catalyst	Yield (%)	Reference
<i>C5 sugar</i>		<i>FF</i>	
Xylose	Lignosulfonic acid	21	Wu et al. (2014)
Xylose	[bmim]Cl-AlCl ₃	79	Wang et al. (2017a)
Arabinose	[bmim]Cl-AlCl ₃	58	Wang et al. (2017a)
Xylose	SCh	60	Wang et al. (2017b)
Xylose	ZrP Monolith	47	Zhu et al. (2016)
Xylose	SO ₄ ²⁻ /Sn-MMT	79	Lin et al. (2017)
<i>FF</i>		<i>TFM</i>	
FF	LF resin	89	Li et al. (2015)
FF	H ₂ SO ₄	70	Subrahmanyam et al. (2017)
FF	Acidic IL	84	Shinde and Rode (2017)
Xylose	Amberlyst-15	28	
Xylose	<i>p</i> -TSA	18	Present Study
Xylose	CS-Fe ₃ O ₄ @SO ₃ H	81	Present Study
Arabinose	(one-pot approach)	70	Present Study

3.5. Catalytic activity comparison

To study the efficiency of CS-Fe₃O₄@SO₃H catalyst, a comparative study was performed considering the studies previously reported in the literature (Table 2). Several researchers have reported a variety of investigations on the conversion of C5 sugars into FF. Wu et al. (2014) reported only 21% yield of FF from xylose using lignosulfonic acid catalyst. Wang et al. (2017a) claimed 79% and 58% yields of FF from xylose and arabinose using Lewis acidic ionic liquids (IL), respectively. Furthermore, over sulfonated char based (SCh) catalyst, Wang et al. (2017b) obtained a 60% FF yield. Whereas, in the presence of ZrP monolith catalyst, Zhu et al. (2016) reported a FF yield as low as 47%. In a different study, the SO₄²⁻/Sn-MMT catalyst was synthesized by Lin et al. (2017) and it was applied for the conversion of xylose into FF resulting in a 79% yield. In the context of TFM synthesis, lignosulfonate-based acidic resin catalyst showed 89% TFM yield from FF (Li et al., 2015). Moreover, in the presence of conc. H₂SO₄, a TFM yield of 70% was obtained (Subrahmanyam et al., 2010). Recently, Shinde and Rode (2017) developed

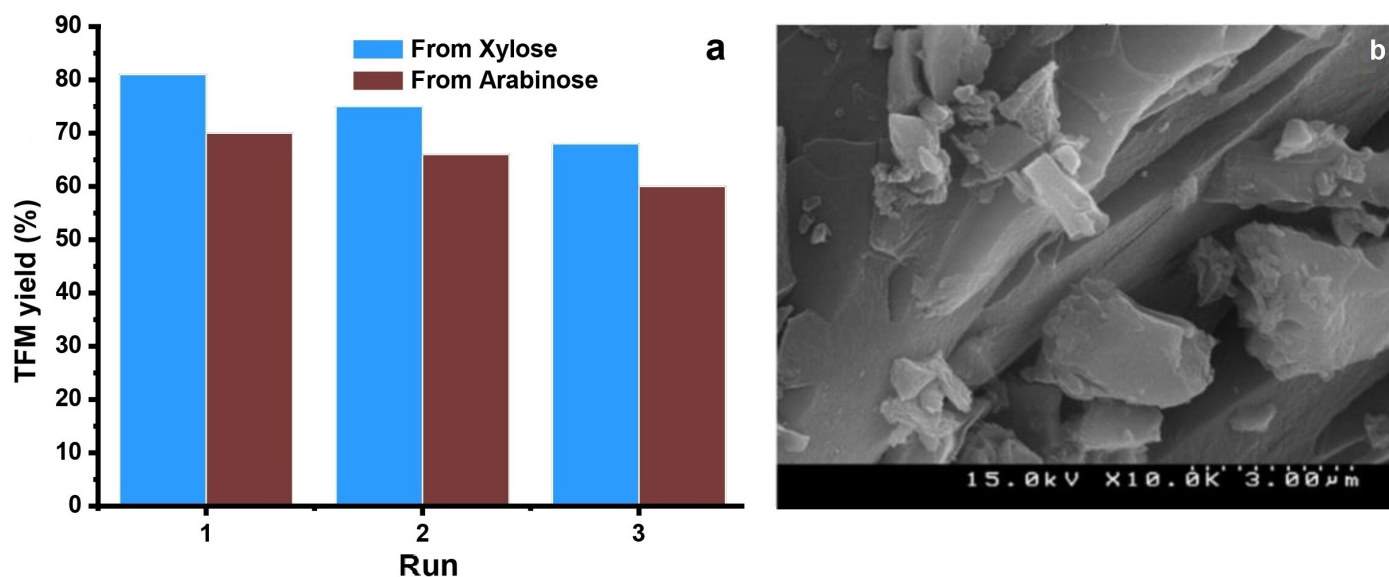


Fig. 4. (a) Variations in TFM yield when $\text{CS-Fe}_3\text{O}_4@\text{SO}_3\text{H}$ catalyst was reused and (b) SEM image of the reused $\text{Fe}_3\text{O}_4@\text{SO}_3\text{H}$ catalyst.

a process for the conversion of FF into TFM with 84% yield by using an acidic IL. Herein, we carried out one-pot reactions using commercially available catalysts such as Amberlyst-15 and *p*-TSA and both catalysts were found considerably less efficient for the formation of TFM under the optimized conditions vs. the catalyst developed in the present investigation (Table 2). Therefore, it could be concluded that the newly synthesized $\text{CS-Fe}_3\text{O}_4@\text{SO}_3\text{H}$ heterogeneous solid acid catalyst was superior for efficient conversion of xylose/arabinose to FF (yields of 84% and 76%, respectively). Moreover, the one pot two-step process resulted in TFM yields of 81% and 70% through xylose/arabinose conversion, respectively. It should also be highlighted that the $\text{CS-Fe}_3\text{O}_4@\text{SO}_3\text{H}$ catalyst was found more favourable in comparison with most of the catalyst systems considered in terms of reaction time, temperature, recovery and reusability of catalyst, and toxicity.

3.6. Reusability of $\text{CS-Fe}_3\text{O}_4@\text{SO}_3\text{H}$ catalyst

Ease of separation and level of reusability of catalysts are among the most important attributes of any catalytic conversion systems. After the first cycle of reaction, the $\text{CS-Fe}_3\text{O}_4@\text{SO}_3\text{H}$ catalyst was separated using an external magnet and was then washed thoroughly with water and ethanol. It was dried in vacuum at 120 °C and used again in the subsequent catalytic reaction cycles. Only slight decreases in TFM yield were observed up to three runs of the reaction (Fig. 4a). Moreover, the SEM image of the reused catalyst was also obtained after three cycles of reaction confirming the similar external morphology of the reused catalyst vs. the freshly prepared one (Fig. 4b and Fig. 1d, respectively). This revealed that the catalyst structure remained unaltered during the reaction and hence, the catalyst could be considered as robust and reusable. The slight decreases recorded in TFM yield after the third cycle might be due to the blockage of active sites by different adsorbed products.

4. Conclusions

A new and efficient magnetic carbonaceous solid acid $\text{CS-Fe}_3\text{O}_4@\text{SO}_3\text{H}$ catalyst was efficiently synthesized and was revealed to possess excellent catalytic activity for the synthesis of TFM from xylose and arabinose using a one-pot approach. The catalyst was synthesized from inexpensive and commercially available CS as carbon source. The acid sites were incorporated on CS-based carbonaceous porous surface could successfully catalyze the dehydration/condensation reactions in an aqueous medium and resulted in a considerable TFM yields. Given the green preparation procedure of the catalyst

as well as its high activity and reusability, it could be industrially used for the conversion of biomass into biofuels.

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Supplementary

S1. Calculation procedure of the density of different functional groups of the developed catalyst

The functional groups over the CS-Fe₃O₄@SO₃H catalyst were investigated using the titration method as explained by Suganuma et al. (2008) and Thombal et al. (2015).

S1.1. Measurement of the total functional groups (-SO₃H, -COOH, and -OH groups)

A sodium hydroxide aqueous solution (0.05 mol.L⁻¹, 30 mL) was added to the catalyst (0.250 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibrations. After centrifugal separation, the supernatant solution was titrated by a hydrochloric acid aqueous solution (0.05 mol.L⁻¹) using phenolphthalein as an indicative.

S1.2. Measurement of -SO₃H plus -COOH functional groups

A sodium bicarbonate aqueous solution (0.05 mol.L⁻¹, 30 mL) was added to the catalyst (0.250 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibrations. After centrifugal separation, the supernatant solution was titrated by a hydrochloric acid aqueous solution (0.05 mol.L⁻¹) using phenolphthalein as an indicative.

S1.3. Measurement of -SO₃H functional group

A sodium chloride aqueous solution (0.05 mol.L⁻¹, 30 mL) was added to the catalyst (0.250 g). The mixture was stirred for 60 min at room temperature under ultrasonic vibrations. After centrifugal separation, the supernatant solution was titrated by a sodium hydroxide aqueous solution (0.05 mol.L⁻¹) using phenolphthalein as an indicative.

S2. Densities of different functional groups of the developed catalyst

Based on the titration results, the -OH groups content was obtained by subtracting the SO₃H plus -COOH groups content from the total functional groups content while the -COOH groups content was obtained by subtracting the SO₃H groups content from the of -SO₃H plus -COOH groups content (Table S1).

Table S1.
The density of different functional groups of the developed catalyst.

Catalyst	Functional group densities (mmol g ⁻¹)		
	COOH	SO ₃ H	OH
CS-Fe ₃ O ₄ @SO ₃ H	0.1	2.3	1.7

S3. Additional optimization results: impact of furan equivalent

Figure S1a and b presents the impact of different furan equivalents on TFM yields through xylose and arabinose conversion, respectively. The crude

reaction mixtures obtained from xylose and arabinose were used for the subsequent condensation reaction.

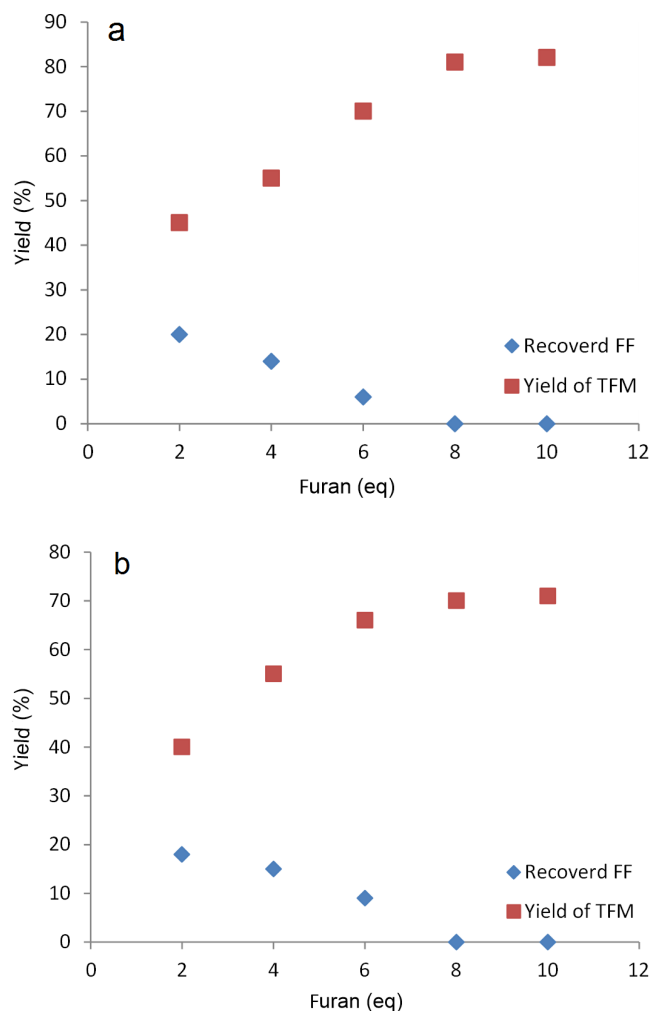


Fig. S1. Variations in TFM yield in response to different furan equivalents through (a) xylose and (b) arabinose conversion catalysed by the developed CS-Fe₃O₄@SO₃H catalyst.

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