Development of TiO₂-Carbon Composite Acid Catalyst for Dehydration of Fructose to 5-Hydroxymethylfurfural

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Abstract: A TiO₂-Carbon (TiO₂C) composite was prepared using the microwave-assisted method and sulfonated using fuming sulfuric acid to produce a TiO₂C solid acid catalyst. The prepared solid acid catalyst was characterised using scanning electron microscopy, Brunauer-Emmett-Teller analysis, Fourier transform infrared spectroscopy, and X-ray diffraction. Crystallinity analysis confirmed that TiO₂C has an anatase structure, while analysis of its morphology showed a combination of spheres and particles with a diameter of 50 nm. The TiO₂C solid acid catalyst was tested for use in the catalytic dehydration of fructose to 5-hydroxymethylfurfural (5-HMF). The effect of reaction time, reaction temperature, catalyst dosage, and solvent were investigated against the 5-HMF yield. The 5-HMF yield was found to be 90% under optimum conditions. The solid acid catalyst is very stable and can be reused for four catalytic cycles. Hence, the material has great potential for use in industrial applications and can be used for the direct conversion of fructose to 5-HMF because of its high activity and high reusability.

Keywords: TiO₂C composite; acid catalyst; dehydration; fructose; 5-Hydroxymethylfurfural

1. Introduction

Increase in the usage of fossil fuels for the production of chemicals and energy has caused not only a rise in greenhouse gas emissions into the atmosphere, but also water pollution, thereby contributing to the growing number of serious health issues. These side effects have spurred researchers to look for alternative ways of producing valuable chemicals and energy using sustainable and renewable resources. Biomass has been identified as a promising resource for the sustainable production of valuable chemical feedstocks and fuels [1]. 5-hydroxymethylfurfural (5-HMF) has been recognised as a key intermediate in the production of biorenewable chemicals [2] and has been classified as a "platform molecule" because it is an important chemical building block used to derive a variety of chemicals, pharmaceuticals, and furane-based polymers [3].

5-HMF is usually synthesised from the dehydration of fructose or glucose using homogeneous organic acids or heterogeneous solid acid catalysts [4]. Although the use of homogeneous catalysts produces high fructose conversion and high dehydrations of 5-HMF, there are drawbacks with regard to separation, recycling, and equipment corrosion [5,6]. Heterogeneous acid catalysts such as mesoporous zirconium phosphate [7,8], sulfonated metal oxides [9], magnetite mixed-metal oxides [10], and functionalised silica nanoparticles [11,12] have been used for the dehydration of fructose to 5-HMF. Although the use of some of these materials has promising results, the studies cited pointed out the

remaining challenge of finding catalysts that are highly active, selective, chemically and structurally stable during repeated use, and do not lead to any side reactions (by-products). Biomass-derived carbonaceous materials were found to be promising candidates for catalytic support application because of their low cost of production and thermal stability [13]. For example, Wang et al. [14] used a sulfonated carbonaceous solid acid catalyst for the dehydration of fructose into 5-HMF in dimethyl sulfoxide (DMSO). Their catalyst was very efficient and effective in that it converted 96.1% of the fructose for a high 5-HMF yield of 93.4%. Zhao et al. [15] further explored a sulfonated carbon sphere solid acid catalyst that converted 100% of the fructose in DMSO solvent at 160 °C for 1.5 h to produce 90% 5-HMF. Wang et al. [16] used C-based solid acid catalysts to catalyse dehydration of fructose in DMSO for 1.5 h at 130 °C to achieve 91.2% 5-HMF. Guo et al. [17] used a lignin-derived carbonaceous catalyst to convert fructose into 5-HMF under microwave irradiation in the mixture of DMSO and ionic liquid at 110 °C for 10 min for a fructose conversion of 98% and a 5-HMF yieldof 84%. Hu et al. [18] explored the use of a magnetic lignin-derived carbonaceous acid catalyst for the catalytic conversion of fructose into 5-HMF in DMSO solvent. Use of the magnetic C-based catalyst achieved a 100% fructose conversion and a 5-HMF yieldof 81.1% under optimum reaction conditions.

Studies have found that the anatase phase of TiO_2 can catalyse the dehydration of carbohydrates such as fructose and glucose into 5-HMF and that the performance of the TiO_2 catalyst is strongly controlled by its morphological and structural properties [3,19–21]. For example, the use of nanostructured TiO_2 remarkably favoured the production of 5-HMF from glucose and fructose [19,20], with its high activity being ascribed to the morphology of the nanoparticles [20].

In this paper, we report the synthesis, characterisation, and application of TiO_2-Carbon sphere (TiO_2C) composite for the catalysis of the dehydration of fructose into 5-HMF in DMSO solvent. To the best of our knowledge, there have been no reports on the use of TiO_2C as a catalyst for the dehydration of fructose into 5-HMF. We synthesised the TiO_2C composites using a microwave-assisted method. Because TiO_2 has redox acidic sites, Bronsted acid sites were introduced by sulfonating the TiO_2C composites with concentrated sulfuric acid. Scanning electron microscopy (SEM), Brunauer-Emmett-Teller (BET) analysis, X-ray diffraction, and Fourier transform infrared (FTIR) spectroscopy were used to characterise the TiO_2C acid catalyst. This solid acid catalyst was tested in DMSO solvent as a catalyst for the dehydration of fructose into 5-HMF. To achieve a higher dehydration of 5-HMF, reaction parameters such as reaction temperature, reaction time, and catalyst amount were optimised. Moreover, the ability to recycle the catalyst was studied to evaluate its catalytic stability.

2. Experimental and Methods

2.1. Materials

All chemicals used for synthesising the TiO_2 nanoparticles (NPs) and TiO_2C composites were purchased from Sigma-Aldrich Corporation (St. Louis, MO, USA). Titanium (IV) isopropoxide (TTIP) and fructose were used as precursors in the preparation of TiO_2 and TiO_2C composites. Polyvinylpyrrolidone (PVP) was used as a surfactant and ammonium hydroxide was used as a reducing agent for the preparation of TiO_2 NPs. Sulfuric acid was used for sulfonating the TiO_2C solid acid catalyst.

2.2. Preparation of TiO_2 Nanoparticles Using the Sol-Gel Method

Ethanol (50 mL) was mixed with 17.79 g of TTIP and stirred for 30 min. PVP (4 g) was added to the mixture, which then was stirred at 70 °C until it was completely dissolved. Next, 4 mL of $NH_3 \cdot 2H_2O$ was added. The solution was heated at 90 °C under reflux conditions for 24 h. The resultant sample was washed with water and dried at 100 °C for 24 h.

2.3. Preparation of Carbon Spheres Using the Microwave-Assisted Method

The carbon precursor (fructose) was mixed with deionised (DI) water and stirred at room temperature (25 to 27 °C) for 2 h. The obtained mixture was transferred into microwavable plastic vessels that were then placed into the ultraclave high-performance microwave reactor and allowed to react at 180 °C for 2 h.

2.4. Preparation of TiO_2C Composites Using the Microwave-Assisted Method

TiO_2 nanoparticles were added to 50 mL of DI water. The solution was sonicated at 30 °C for at least 1 h, after which the fructose was added. The pH of the solution was adjusted to 2. The solution was stirred at room temperature (25 to 27 °C) for 2 h and then microwaved in the ultraclave high-performance microwave reactor for another 2 h at 180 °C. The resultant sample was washed three times with DI water, dried at 150 °C for 24 h, and then calcined at 500 °C for 2 h. Different amounts of TiO_2 nanoparticles (1, 5, and 10%) were loaded onto the carbon spheres. For example, to prepare the 1%TiO_2C nanocomposite, 0.1 g of TiO_2 nanoparticles was added to 9.9 g of fructose, whereas to prepare the 5%TiO_2C and 10%TiO_2C, the mass ratio of TiO_2 nanoparticles to fructose was 0.5:9.5 and 1:9, respectively. The TiO_2C composites loaded with 1, 5, and 10% TiO_2 were denoted as 1%TiO_2C, 5%TiO_2C, and 10%TiO_2C, respectively.

2.5. Preparation of the Sulfonated Carbon and TiO_2C Acid Catalysts

TiO_2C was sulfonated by adding 1 g of TiO_2C composite to 25 ml of concentrated sulfuric acid and stirring the solution at 120 °C for 24 h under reflux conditions. The sulfonated samples, denoted as TiO_2C_S, were washed with DI water and dried at 150 °C for 24 h. The carbon spheres were sulfonated using the same method and were denoted as C_S.

2.6. Surface Acid Measurement Tests

A total of 100 mg of C_S and TiO_2C_S composite acid catalysts was mixed with 50 ml of DI water and 40 ml of 0.01 M NaOH and stirred at room temperature (25 to 27 °C) overnight [22]. The solution was filtered and titrated with 0.1 N of oxalic acid using phenolphthalein as the indicator.

2.7. Characterisation

Elemental composition and surface morphology analyses were conducted using the AURIGA® scanning electron microscope (Zeiss, Oberkochen, Germany). The crystallinity and phase composition were investigated using the PanAlytical X'Pert Pro (Panalytical Ltd., Eindhoven, The Netherlands). The functional groups of the catalysts were measured in the wavelength range of 550–4000 cm^{-1} using a Spectrum 100 FTIR spectrometer (PerkinElmer, Waltham, MA, USA). The specific surface area, pore volume, and pore size were measured using the ASAP 2020 BET analysis system (Micromeritics Instruments Corp., Norcross, GA, USA).

2.8. Catalytic Testing

Fructose (0.5 g), DMSO (6 ml), and catalyst (0.1 g) were placed in a vessel and allowed to react for 1 h at 120 °C using the ultraclave high-performance microwave reactor. After the reaction, the solution was centrifuged to separate the solid catalyst particles from the liquid, and the supernatant liquid was analysed using a Lambda UV-Vis spectrometer Model 750s (PerkinElmer, Shelton, CT, USA) at the wavelength of 284 nm.

2.9. Reusability Studies

Reusability of the materials was studied using the dehydration of fructose into 5-HMF in DMSO as an illustrative reaction. The C_S and TiO_2C_S composite acid catalysts were allowed to react for 1 h in separate vessels and then were separated from the solution by centrifugation. The recovered

catalysts were then washed thoroughly with DI water and ethanol and dried for 4 h at 90 °C. This process was repeated four times, with the 5-HMF yield calculated each time.

2.10. Hot Filtration Tests

The 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S acid catalysts were used to perform hot filtration tests to determine the heterogeneous nature of the acid catalyst. In a typical procedure, 0.5 g of fructose and 0.1 g of TiO$_2$C_S were added to 6 ml of DMSO and allowed to react for 30 min using the ultraclave high-performance microwave reactor. After the reaction, the solution was allowed to cool down and then was centrifuged to separate the catalyst from the reaction mixture. The solution was analysed using a UV-Vis spectrometer at a wavelength of 284 nm. The same reaction was repeated for 1 h using the solution filtrate without adding the substrate.

3. Results and Discussion

3.1. BET Surface Area and Pore Volume of the Catalysts

The BET surface area and pore volume of the carbon spheres and the various compositions of the TiO$_2$C composites are presented in Table 1. The carbon spheres had a surface area of 517 m^2/g before sulfonation. However, a reduction in surface area was observed after adding TiO$_2$ NPs to the carbon due to TiO$_2$ NPs blocking some of the micropores of the carbon. The TiO$_2$C composite loaded with the lowest dosage of TiO$_2$ NPs (i.e., 1%TiO$_2$C) had a larger surface area and pore volume of 413 m^2/g and 0.26 cm^3/g, respectively, than the composites loaded with higher amounts of TiO$_2$ (i.e., 5%TiO$_2$C and 10%TiO$_2$C). The surface area of the TiO$_2$C composite decreased when a high loading of TiO$_2$ NPs was introduced onto the carbonaceous support. The 1%TiO$_2$C composite had the highest pore volume of 0.26 cm^3/g compared to that of 5%TiO$_2$C and 10%TiO$_2$C composites. Both the surface area and the pore volume were affected by functionalising the carbon spheres and TiO$_2$C with concentrated sulfuric acid. After sulfonation, the surface area of the carbon spheres decreased from 517 to 167 m^2/g and that of the 1%TiO$_2$C, 5%TiO$_2$C, and 10%TiO$_2$C composites decreased from 413 to 83, 273 to 61, and 202 to 59 m^2/g, respectively. Pore volume also decreased. The reduction in surface area and pore volume might be attributed to the SO$_3$H groups that were attached to the pores of the carbon spheres and TiO$_2$C composites during sulfonation. Other researchers reported similar results [21,22]. For example, Tamborini et al. [21] synthesised sulfonated porous carbon materials and used them for the production of biodiesel. The surface areas of the different synthesised carbons (PC100S and PC200S) were 630 and 695 m^2/g, respectively. The sulfonation process decreased the surface area of PC100S to 470 m^2/g and that of PC200S to 140 m^2/g. The pore volume of the carbon materials also decreased from 0.92 to 0.77 cm^3/g and from 1 to 0.34 cm^3/g, respectively. Sulfonation corroded the microporosity and mesoporosity of these carbon materials. Liu et al. [22] prepared a carbon-based acid catalyst and used it for the esterification of acetic acid with ethanol. After sulfonation, the surface area and pore volume of the activated carbon decreased from 751 to 602 m^2/g and from 0.47 to 0.38 cm^3/g, respectively. Their findings suggested that SO$_3$H groups were grafted onto the pore spaces of the activated carbons.

Table 1. Textural properties and hot filtration results of carbon spheres and TiO$_2$C nanocomposites.

Catalyst before Sulfonation			Catalyst after Sulfonation		
	S_{BET} (m^2/g)	V_p (cm^3/g)		S_{BET} (m^2/g)	V_p (cm^3/g)	Sulfonic Groups (m·molg^{-1}) [a]
C	517	-	C_S	167	-	1.34
1%TiO$_2$C	413	0.26	1%TiO$_2$C_S	83	0.07	1.46
5%TiO$_2$C	273	0.13	5%TiO$_2$C_S	61	0.04	1.55
10%TiO$_2$C	202	0.10	10%TiO$_2$C_S	59	0.03	1.49

C: Carbon; S_{BET}: Surface Area; V_p: Pore Volume; S_: Sulfonated; [a] Attained by titration with NaOH.

The acid strength of C_S, 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S was calculated to be 1.46, 1.55, 1.49, and 1.36 mmol g^{-1}, respectively, as seen in Table 1. The acid distribution results confirmed that SO$_3$H acid sites were introduced onto the surface of the prepared catalysts, verifying the strong adsorption bands of the S=O group at 1180 and 1008 cm^{-1}, which were associated with the SO$_3^-$ groups in the FTIR spectra discussed in Section 3.3.

The heterogeneous nature of the 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S acid catalysts was evaluated using hot filtration tests conducted at optimum conditions. The results showed that leaching of SO$_3$H functional groups did not occur during the dehydration of fructose to 5-HMF. The 5-HMF dehydration was about 80% after 30 min of reaction. The reaction was repeated again for 1 h and showed that the HMF dehydration did not improve beyond 80%. These findings confirmed that the TiO$_2$C_S acid catalysts are heterogeneous and that the functional groups were strongly attached to the surface of the TiO$_2$C_S catalysts, so leaching did not occur.

3.2. Surface Morphology

The SEM images of the neat carbon and neat TiO$_2$C composites are shown in Figure 1a–d, and those of the C_S and TiO$_2$C_S acid catalysts are shown in Figure 1e–h. The neat carbon was spherical and had a smooth surface, with the spheres agglomerated and interconnected (Figure 1a). The neat 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S composites consisted of a combination of interconnected spheres and small TiO$_2$ particles which did not have a definite shape, and were aggregated (Figure 1b–d). Moreover, a high amount (5 and 10 wt.%) of TiO$_2$ NPs loading promoted the formation of irregular TiO$_2$ particles in the TiO$_2$C composites. After sulfonation, the particles were found to have shrunk, as seen in Figure 1f–h, whereas in a case of C_S the spheres were found to have enlarged as shown in Figure 2e.
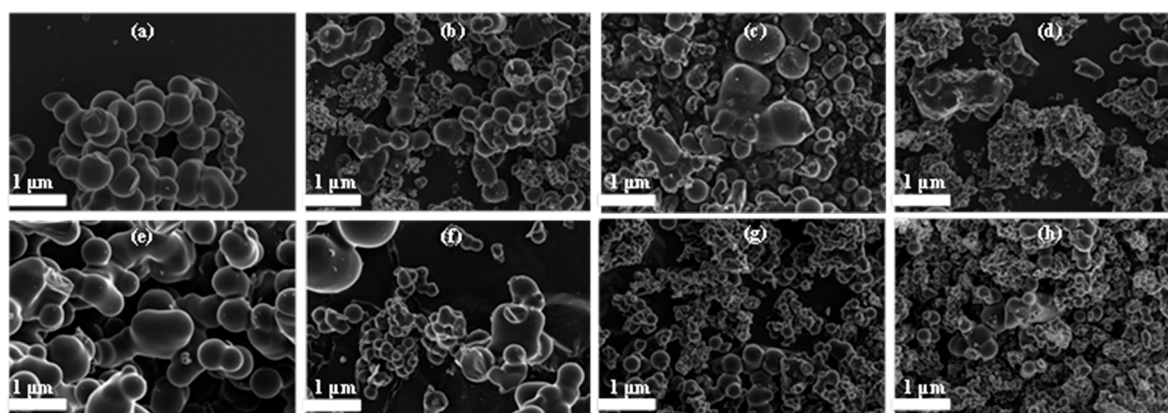

Figure 1. SEM low magnification images of (**a**) neat C, (**b**) neat 1%TiO$_2$C, (**c**) neat 5%TiO$_2$C, (**d**) neat 10%TiO$_2$C, (**e**) C_S solid acid catalyst, (**f**) 1%TiO$_2$C_S solid acid catalyst, (**g**) 5%TiO$_2$C_S solid acid catalyst, and (**h**) 10%TiO$_2$C_S solid acid catalyst.

Figure 2 shows the high magnification SEM images of (a) C_S solid acid catalyst, (b) 1%TiO$_2$C_S, (c) 5%TiO$_2$C_S, (d) 10%TiO$_2$C_S and (e) sulfonated TiO$_2$. From Figure 2a, we can see that the C_S solid acid catalyst had a smooth surface, whereas the 1%TiO$_2$C_S and 5%TiO$_2$_S showed the presence of small traces of TiO$_2$ particles which were deposited onto the carbon surface. In the 10%TiO$_2$C_S sample (Figure 2d) TiO$_2$ particles were deposited on the surface of the carbon. However, these TiO$_2$ particles were not homogeneously distributed onto the surface of the carbon. In the sulfonated TiO$_2$ sample (Figure 2e); SEM revealed that TiO$_2$ particles had irregular shaped and were agglomerated.
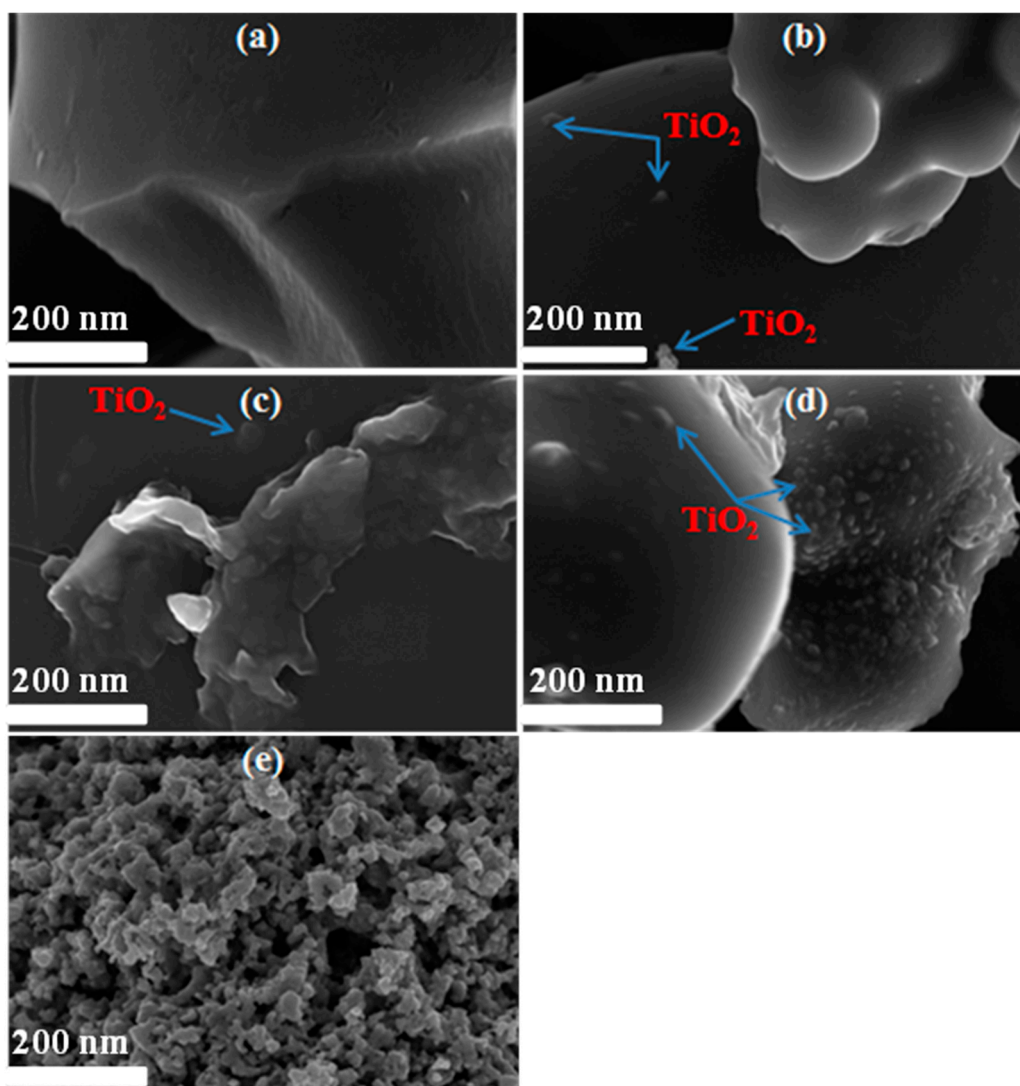
Figure 2. SEM high magnification images of (**a**) C_S solid acid catalyst, (**b**) 1%TiO$_2$C_S solid acid catalyst, (**c**) 5%TiO$_2$C_S solid acid catalyst, (**d**) 10%TiO$_2$C_S solid acid catalyst and (**e**) sulfonated TiO$_2$.

The energy-dispersive spectroscopy (EDS) spectra of the neat carbon and neat TiO$_2$C composites are shown in parts (a) to (d) of Figure 3, and those of the carbon spheres and TiO$_2$C after sulfonation are shown in parts (e) to (h) of Figure 3. The EDS spectrum of the carbon spheres contains only C and O peaks, whereas that of the composite samples contains the Ti peak, confirming that TiO$_2$ was present in the samples. The elemental weight percent of C decreased with an increase in TiO$_2$ loading. After sulfonating the carbon, the C, O, and S peaks are present in the spectrum (Figure 3e), indicating that the carbon spheres were neat and no impurities were detected in the sample. The spectra of the TiO$_2$C_S acid catalysts [parts (f) to (h) of Figure 3] showed the presence of C, O, Ti, and S, and the elemental weight percentage of Ti increased with an increase in the loading percentage of TiO$_2$. However, the weight percentage of C decreased with an increase in the loading percentage of TiO$_2$. No other impurity elements were found in the prepared solid acid catalysts. The presence of S in all the solid acid catalysts indicated that the samples were successfully functionalised with sulfuric acid. Elemental composition analysis revealed that all the prepared acid catalysts contained sulfonic acid in the form of SO$_3$H groups [23], further proving the presence of sulfonic groups, as indicated in Table 1. Wang et al. [14] also confirmed the presence of sulfonic groups on the surface of carbon materials after sulfonation. The TiO$_2$C_S composites had C, O, Ti, and S, and their elemental weight percent of Ti

increased with an increase in the loading percentage of Ti. However, the weight percent of C decreased with an increase in the loading percentage of Ti.
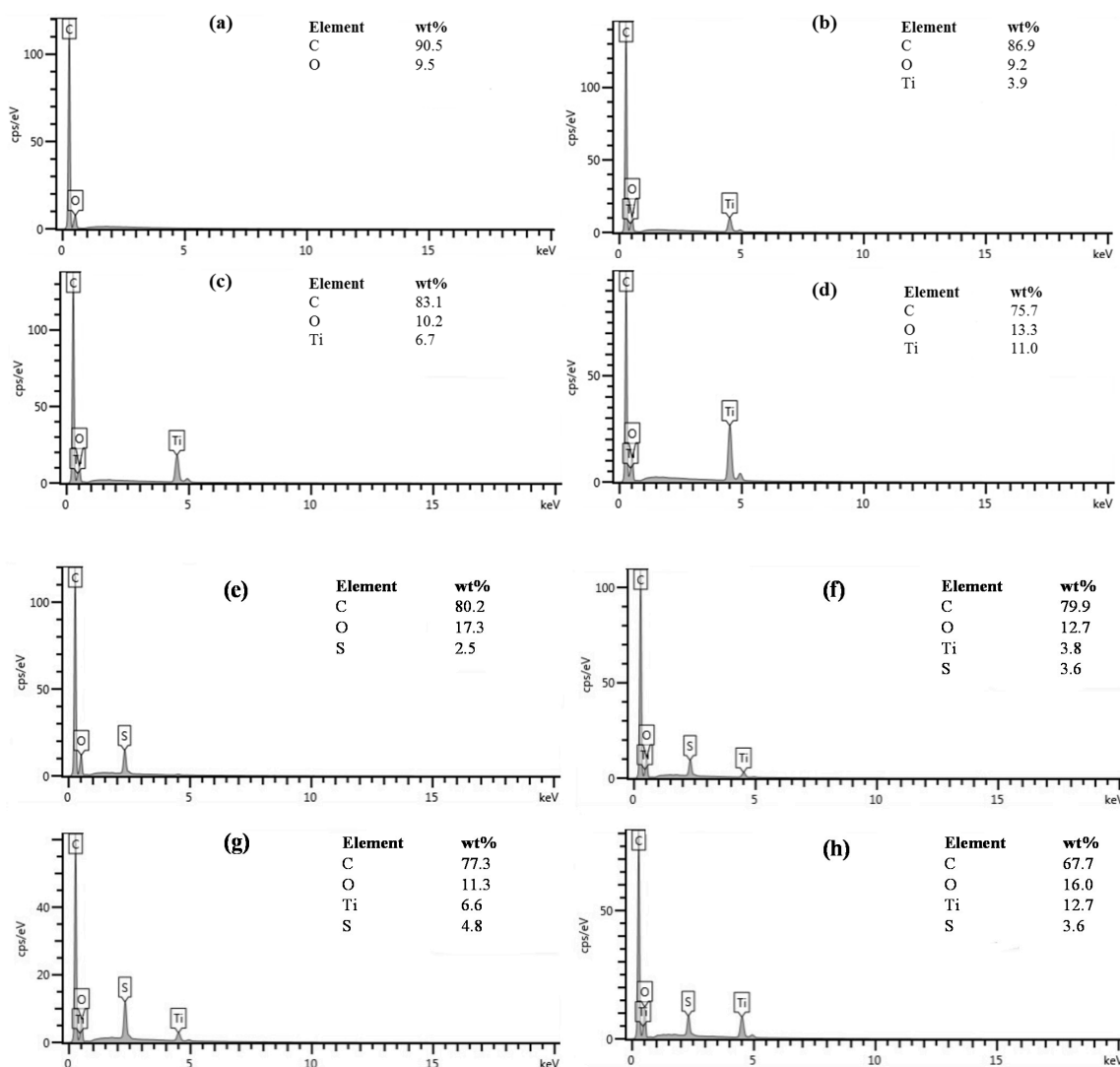

Figure 3. EDS spectra and elemental composition of (**a**) neat C, (**b**) neat 1%TiO$_2$C, (**c**) neat 5% TiO$_2$C, (**d**) neat 10% TiO$_2$C, (**e**) C_S solid acid catalyst, (**f**) 1%TiO$_2$C_S solid acid catalyst, (**g**) 5% TiO$_2$C_S solid acid catalyst, and (**h**) 10% TiO$_2$C_S solid acid catalyst.

3.3. Chemical Analysis Using FTIR

The FTIR spectra of the neat, calcined, and sulfonated carbon spheres are shown in Figure 4a. The presence of oxygen groups is demonstrated by the bands at 3000–3600 and 1710 cm^{-1}, which were attributed to –OH stretching and C=O vibrations, respectively [3,24]. The 875–750 cm^{-1} band was assigned to the aromatic C–H group, and the presence of aromatic rings was confirmed by the band at 1620 cm^{-1}, which was assigned to C=C vibrations [24]. Additional bands at 1180 and 1008 and 1106−1168 cm^{-1} were observed in the spectrum of the sulfonated carbon spheres. These bands were assigned to the symmetric stretching vibration of S=O groups, which are associated with the SO$_3^-$ groups [25] and C=S stretching [26], respectively as shown in Figure 4a. These sulfonic peaks in the spectrum of the sulfonated carbon spheres indicate that -SO$_3$H functional groups were attached to the carbon spheres. The FTIR spectra of the neat, calcined, and sulfonated 1%TiO$_2$C, 5%TiO$_2$C, and 10%TiO$_2$C (Figure 4b–d) show bands at 1700 and 1200 cm^{-1}, which were attributed to the C=O and

C–O stretching of the carboxyl group [27]. A strong adsorption band of the S=O group at 1008 cm^{-1}, which was associated with the SO_3^- groups, was observed.
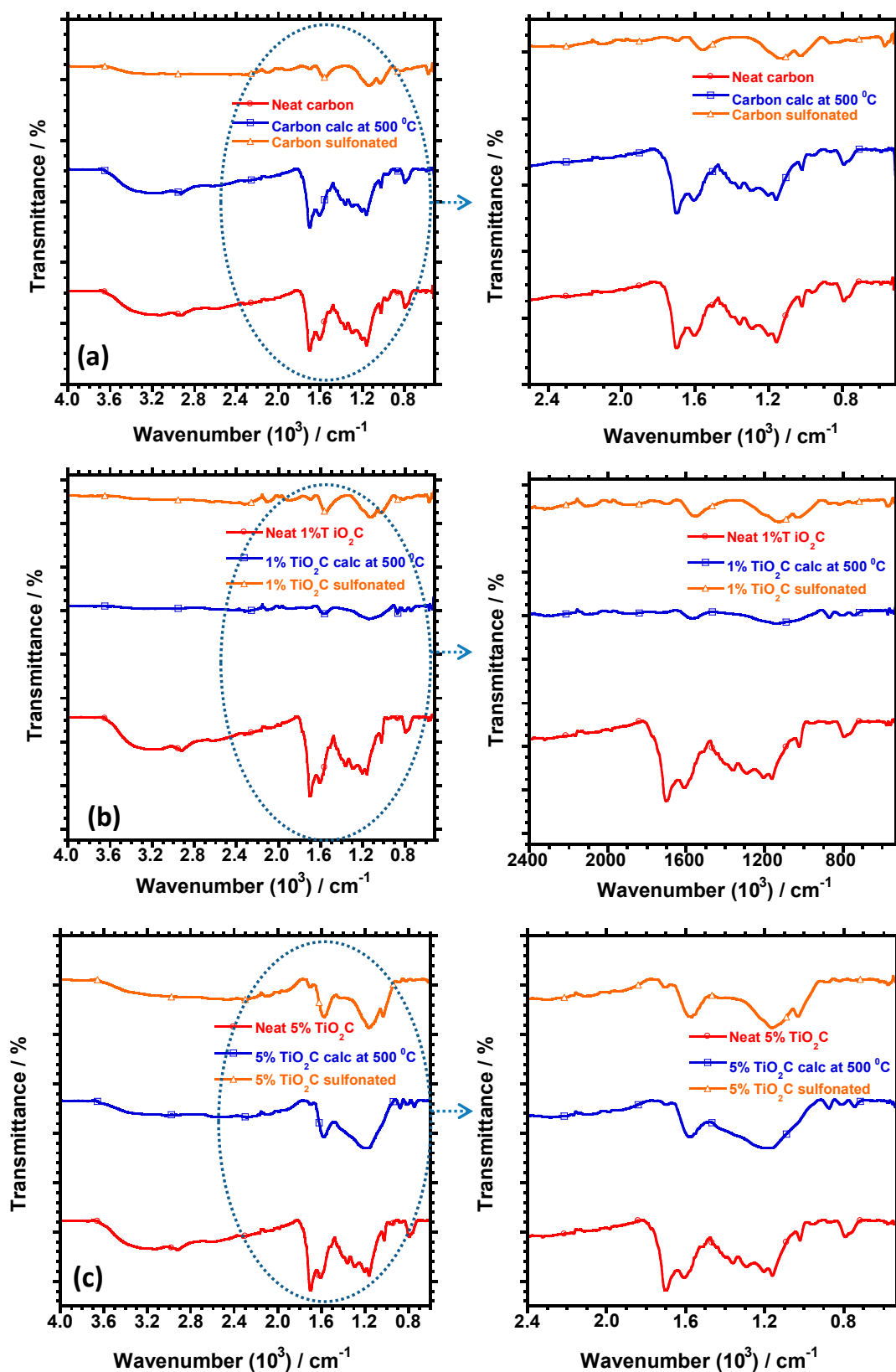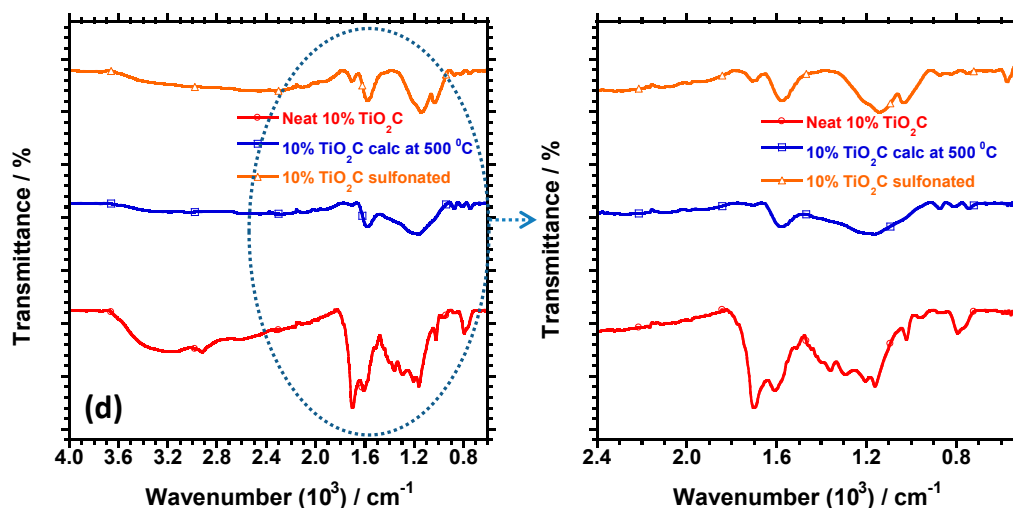

Figure 4. *Cont.*

Figure 4. FTIR spectra of neat, calcined and sulfonated (**a**) carbon, (**b**) 1%TiO$_2$C, (**c**) 5%TiO$_2$C, and (**d**) 10%TiO$_2$C.

3.4. Structural Characterisation Using XRD

The XRD patterns of the calcined carbon spheres and TiO$_2$C composites are shown in Figure 5a. The XRD pattern of the neat carbon spheres showed broad peaks at 25° and 43°, which were indexed to the [002] and [100] characteristic phases of amorphous carbonaceous material, whereas the TiO$_2$C sample which was loaded with the least dosage of TiO$_2$ (1%TiO$_2$C), was found to be amorphous, due to the effect of high concentration of the carbon which was present in the sample. The XRD pattern of the crystalline structure of the 5%TiO$_2$C and 10%TiO$_2$C composites had sharp peaks at 25.2°, 37.83°, 48.2°, 54.8°, 62.2°, and 70.2°, which were indexed to the [101], [004], [200], [105], [204], and [116] phases of anatase TiO$_2$ [28]. After sulfonation, the peaks for the carbon spheres and 1%TiO$_2$C shifted, as shown in Figure 5b. Moreover, the acid treatment (sulfonation) caused the [100] plane peak to disappear. The 5%TiO$_2$C and 10%TiO$_2$C composites were not affected by the sulfonation.
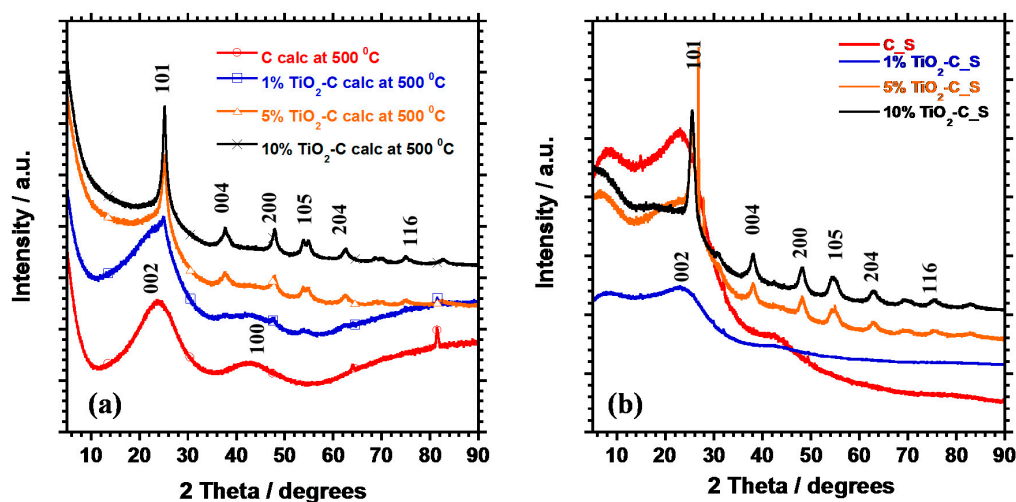

Figure 5. XRD results for carbon spheres and TiO$_2$C composites (**a**) that were calcined at 500 °C and (**b**) after sulfonation.

3.5. Catalytic Testing

3.5.1. Effect of Different Solvents on the Dehydration of Fructose into 5-HMF

Dehydration of fructose into 5-HMF was tested using different alcoholic solvents (such as isopropanol, ethanol, and methanol), water, and DMSO at 120 °C for 60 min (Table 2). All the

alcoholic solvents produced a low 5-HMF yield of <12% on all the solid catalysts tested for this reaction. Water was also found to be an ineffective solvent. DMSO was the most effective solvent. The HMF yield was 84% for the carbon solid acid catalyst, 91% for 1%TiO$_2$C_S, 92% for 5%TiO$_2$C_S, and 95% for 10%TiO$_2$C_S. Thus, the HMF dehydration increased as the TiO$_2$ content increased. These results suggest that DMSO is a suitable solvent for use in the dehydration of fructose into 5-HMF when using TiO$_2$C solid acid catalysts. DMSO acted both as a solvent and as a reaction mediator; hence a high dehydration of 5-HMF was achieved.

Table 2. Dehydration of fructose in different solvents.

Catalyst	HMF Dehydration (%) [UV-Vis at the Measured Absorbance of 284 nm]				
	Methanol	DI Water	Ethanol	Isopropanol	DMSO
C	3	5	11	1	84
1%TiO$_2$C	3	6	4	9	91
5%TiO$_2$C	3	1	6	0	92
10%TiO$_2$C	0	4	12	11	95

Reaction conditions: Substrate, fructose; catalyst amount, 0.1 g; temperature, 120 °C; time, 60 min.

Table 3 shows a comparison of the TiO$_2$C composite acid catalyst synthesised in this work with other catalysts reported in published works on dehydration of fructose into 5-HMF in DMSO using the microwave-assisted method. We found that our designed TiO$_2$C_S acid catalysts produced the highest 5-HMF yield. The highest 5-HMF yield that we achieved at 120 °C, a temperature lower than those used in other studies, was 91% for 1%TiO$_2$C_S and 92 and 95% for 5%TiO$_2$C_S and 10%TiO$_2$C_S, respectively. To our knowledge, this is the first report of the use of TiO$_2$C_S composites as effective solid acid catalysts for the conversion of fructose into 5-HMF using the microwave-assisted method. De et al. [19] used mesoporous TiO$_2$ nanomaterial to catalyse the dehydration of D-fructose into 5-HMF in DMSO solvent under microwave-assisted heating. This reaction was conducted at 130 °C for 2 min for a 49.2% 5-HMF yield was achieved. Dutta et al. [15] also used mesoporous TiO$_2$ nanoparticles for the same reaction at 140 °C for 5 min and reported a yield of53.4%. Use of carbonaceous acid catalysts for this reaction achieved a 100% conversion of fructose and 90% 5-HMF yield at 160 °C for 1.5 h. Wang et al. [16] used carbon-based solid acid catalysts to catalyse the dehydration of fructose into 5-HMF at 130 °C for 1.5 h for a 5-HMF yield of about 91.2%. Hu et al. [18] explored a magnetic lignin-derived carbonaceous acid catalyst for the catalysed conversion of fructose into 5-HMF and achieved a 5-HMF yield of 81.1% with 100% fructose conversion.

Table 3. Comparison of results of the dehydration of fructose (substrate) into 5-HMF in DMSO using carbonaceous and TiO$_2$-based solid acid catalysts.

Catalyst	Catalyst Mass (g)	Substrate Mass (g)	T (°C)	Time (min)	5-HMF Yield (%)		Ref.
					Uv-Vis [a]	HPLC [b]	
C_S	0.1	0.5	120	60	84	-	This work
1%TiO$_2$C_S	0.1	0.5	120	60	91	-	This work
5%TiO$_2$C-S	0.1	0.5	120	60	92	-	This work
10%TiO$_2$C_S	0.1	0.5	120	60	95	-	This work
TiO$_2$	0.05	0.1	130	2	49.5	47.8	[19]
TiO$_2$	0.1	0.05	140	5	53.4	-	[20]
CS	0.1	0.5	160	90	-	90	[15]
C	0.4	0.5	130	90	-	91.2	[16]
Magnetic lignin-derived carbon (MLC)-SO$_3$H	0.05	0.1	130	40	-	81.1	[18]

[a] 5-HMF dehydration was calculated by UV-vis at the measured absorbance of 284 nm; [b] 5-HMF dehydration measured by HPLC.

3.5.2. Effect of Reaction Temperature on HMF Dehydration

The effect of reaction temperature on the catalytic transformation of fructose to HMF was carried out at 25, 60, 80, 100 and 120 °C. The reaction was conducted using 1%TiO$_2$C_S, 5%TiO$_2$C_S,

10%TiO$_2$C_S, C_S solid acid catalysts and without the catalyst (non-catalytic reaction). The results are shown in Figure 6, which suggests that no 5-HMF was formed when the reaction was carried out in the absence of a catalyst on all the reaction temperatures that were studied. For the carbon solid acid catalyst and reaction temperature of 25 °C, the 5-HMF yield was <8%. When the temperature was raised to 60 °C, the 5-HMF yield slightly increased to 35%. At 80 °C, the 5-HMF yield improved to 71%. The highest 5-HMF yield of 85% was achieved at 120 °C. The effect of reaction temperature was also tested using the 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts. The 5-HMF yield was low when the reaction was conducted at 25 °C, then increased as the reaction temperature increased. The highest HMF yields of 91, 92, and 95% were achieved at 120 °C with the use of 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts, respectively. Thus, the best temperature for 5-HMF production using these composite catalysts was 120 °C. Compared to the performance of the carbon solid acid catalyst, an improved HMF yield was achieved with the use of 1, 5, and 10%TiO$_2$C_S solid acid catalysts.
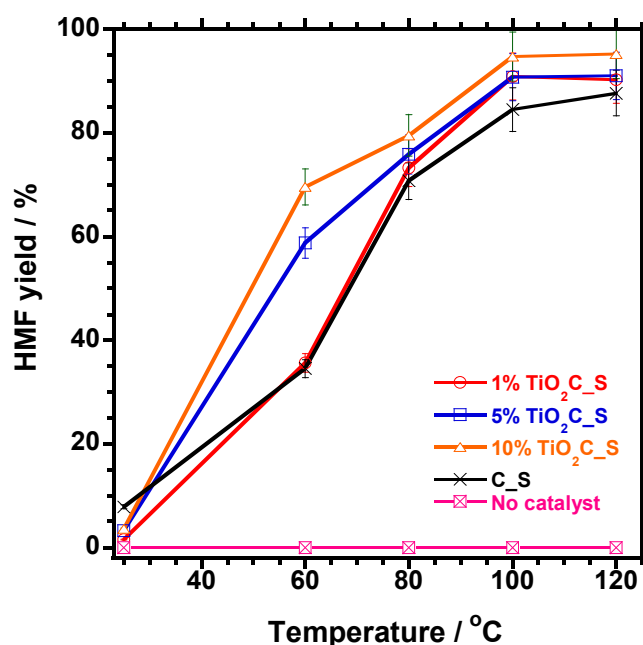

Figure 6. Effect of reaction temperature on fructose dehydration into HMF using sulfonated carbon and TiO$_2$C composite catalysts in DMSO solvent.

3.5.3. Effect of Reaction Time on 5-HMF Dehydration

The effect of reaction time on the catalysed dehydration of fructose into 5-HMF was studied using different times of 15, 30, 60, and 120 min. The reaction was conducted using the prepared solid acid catalysts and no catalyst (non-catalytic reaction). The results are shown in Figure 7. No 5-HMF was formed when the reaction was carried out without a catalyst for all four reaction times. When the reaction was performed with the C_S solid acid catalyst, increasing the reaction time from 15 to 30 min improved the 5-HMF yield from 25% to 46%. The HMF dehydration increased rapidly to 85% after conducting the reaction for 60 min. However, performing the reaction for 120 min caused a slight drop in the 5-HMF yield to 83%. When conducting the dehydration reaction using 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts, increasing the reaction time from 15 to 30 min increased the 5-HMF yield from 27 to 49%, 28 to 58%, and 29 to 68%, respectively. Increasing the reaction time to 60 min significantly improved the 5-HMF yield to >90% for all the TiO$_2$C composite acid catalysts. Finally, for a reaction time of 120 min, the HMF dehydration for 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts was calculated to be 88, 92, and 93%, respectively.
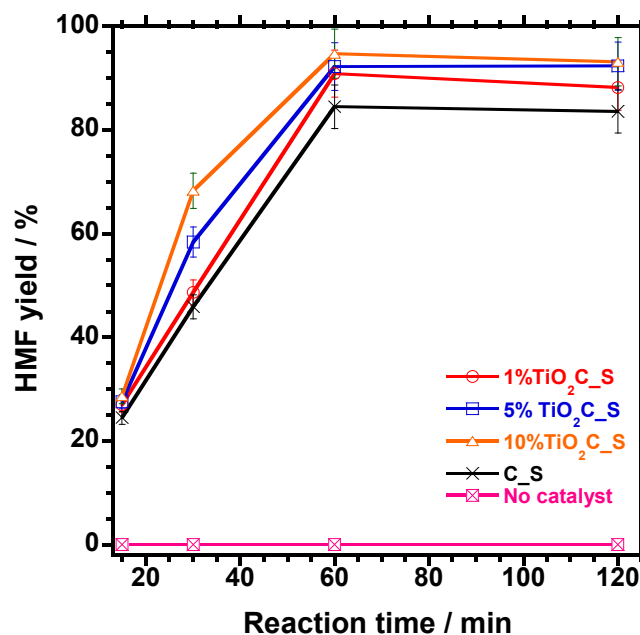
Figure 7. Effect of reaction time on the dehydration of fructose into HMF in DMSO solvent.

3.5.4. Effect of Catalyst Amount on HMF Dehydration

The effect of the amount of catalyst on the 5-HMF yield was studied, with the results presented in Figure 8. The reaction was carried out using catalyst dosages of 0.02, 0.05, 0.1, and 0.2 g. The results indicated that no 5-HMF was formed when this reaction was conducted in the absence of a catalyst on all the catalyst dosages that were studied. The 5-HMF yield increased from 34 to 59% when the amount of the C_S solid acid catalyst increased from 0.02 to 0.05 g under the same reaction conditions. An increase in the catalyst dosage to 0.1 g increased the 5-HMF yield to 85%. However, increasing the catalyst dosage to 0.2 g resulted in a reduction of the 5-HMF yield to 82%. The effect of catalyst concentration was also tested using the 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts. An increase in the catalyst dosage from 0.02 to 0.1 g drastically improved the 5-HMF yield of the 1%TiO$_2$C_S, 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts to 91, 92, and 95%, respectively. However, when the catalyst dosage increased to 0.2 g, the 5-HMF yield of the 5%TiO$_2$C_S, and 10%TiO$_2$C_S solid acid catalysts slightly decreased to 91 and 92% respectively, whereas in a case of the 1%TiO$_2$C_S the 5-HMF yield increased to 93%. This decrease in 5-HMF dehydration at a high catalyst dosage for the 5%TiO$_2$C_S and 10%TiO$_2$C_S, could be attributed to the excess acid active sites that promote both the dehydration reaction and the formation of by-products such as humins [29]. The 5-HMF yields did not increase with an increase in catalyst dosage for the C_S, 5%TiO$_2$C_S and 10%TiO$_2$C_S solid acid catalysts.
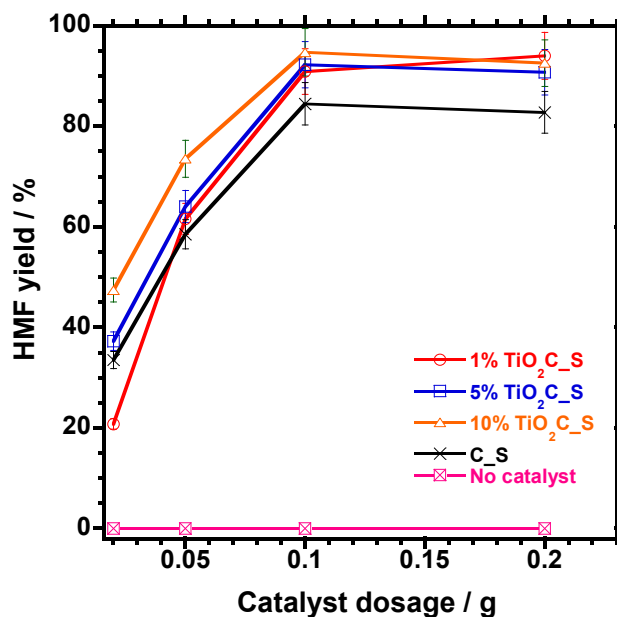
Figure 8. Effect of catalyst dosage on the dehydration of fructose into HMF in DMSO solvent.

3.5.5. Reusability of the Catalyst

The reusability of the catalysts was studied, with the results presented in Figure 9. After the first run, the 5-HMF yields were 94, 97, and 93% for 1%TiO_2C_S, 5%TiO_2C_S, and 10%TiO_2C_S, respectively. The 5-HMF yield slightly decreased after the fourth run. The 5-HMF yield of the 1%TiO_2C_S and 10%TiO_2C_S composite acid catalysts decreased by 3% and that of 5%TiO_2C_S decreased by 5%. These results indicate that the TiO_2C composite acid catalysts are highly stable and can be reused for the dehydration of fructose.
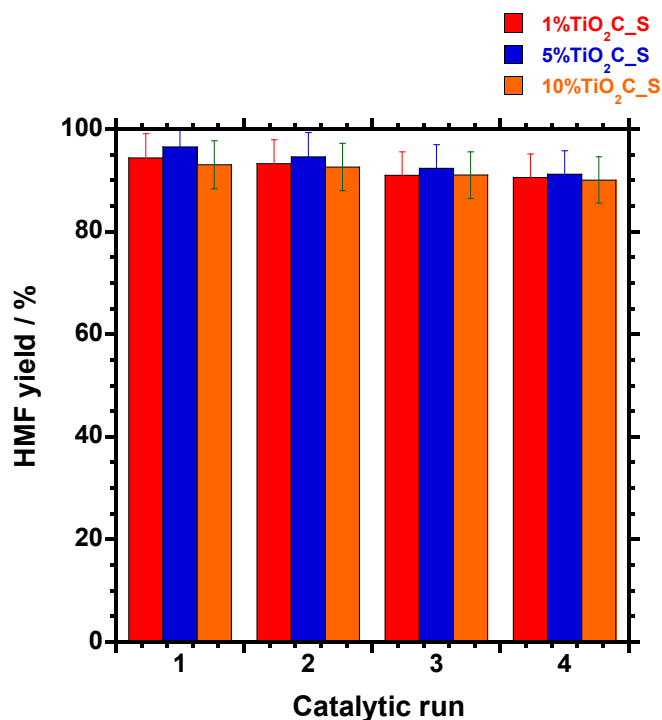

Figure 9. Recycling of the 1%TiO_2C_S, 5%TiO_2C_S, and 10%TiO_2C_S acid catalysts used in the dehydration of fructose into HMF. Conditions: reaction time = 60 min, reaction temperature = 120 °C, catalyst concentration = 0.1 g, amount of fructose = 0.5 g, volume of DMSO = 6 mL).

4. Conclusions

TiO$_2$C solid acid catalysts were successfully prepared using the microwave-assisted method and then sulfonated with concentrated sulfuric acid. Microwave heating increases the rate of dehydration of fructose. The dehydration of fructose is closely related to the acidity of the catalyst. Among the solvents tested for use in the dehydration of fructose into 5-HMF, DMSO performed the best in terms of 5-HMF dehydration. The reaction temperature, reaction time, and catalyst dosage were found to have an effect on the 5-HMF dehydration. The solid acid catalysts synthesised in this work were highly stable and heterogeneous. Moreover, this study was the first time such TiO$_2$C solid acid catalysts were used for dehydrating fructose into 5-HMF.

Author Contributions: M.M.S. design the concept and wrote the first draft of manuscript. R.M. went through manuscript and provided comments. S.S.R. critically reviewed and corrected the manuscript.

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