Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Bifunctional carbon Ni/NiO nanofiber catalyst based on 5-sulfosalicylic acid for conversion of C5/C6 carbohydrates into ethyl levulinate

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Section 1. Experimental

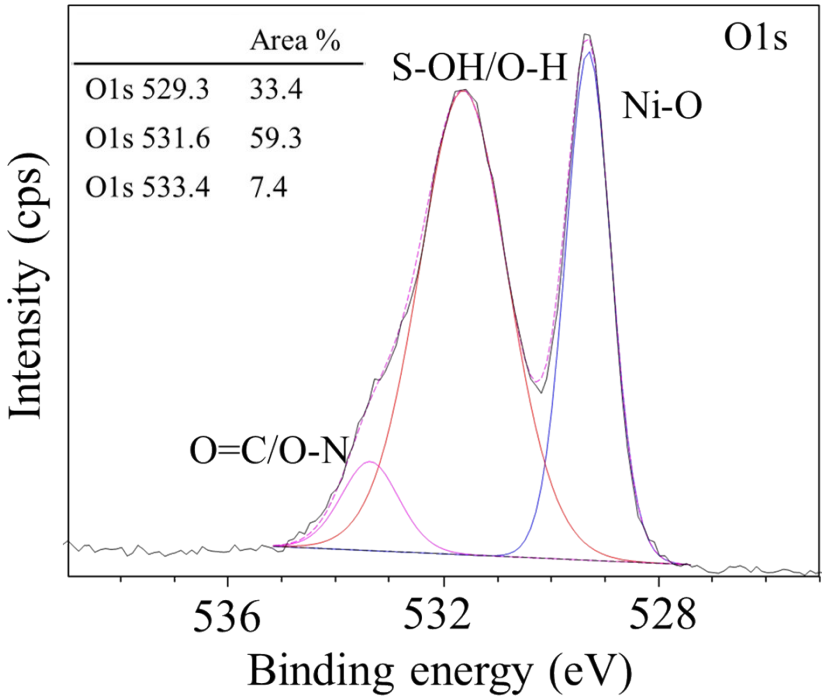

Figure S1. XPS spectra, O 1s region of as-prepared bifunctional carbon Ni/NiO nanofiber catalyst.

Catalyst characterization (SEM images)

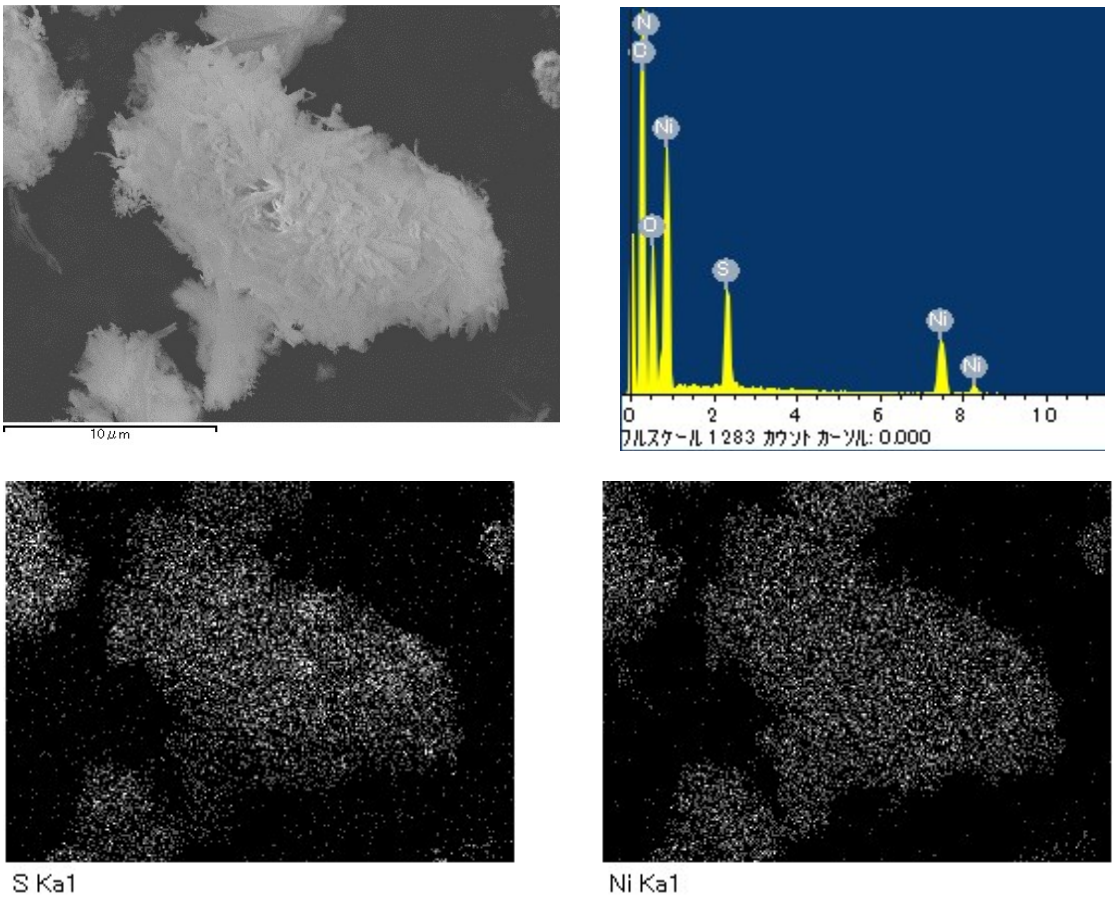

Figure S2. SEM images of as-prepared bifunctional carbon Ni/NiO nanofiber catalyst and corresponding EDX maps.

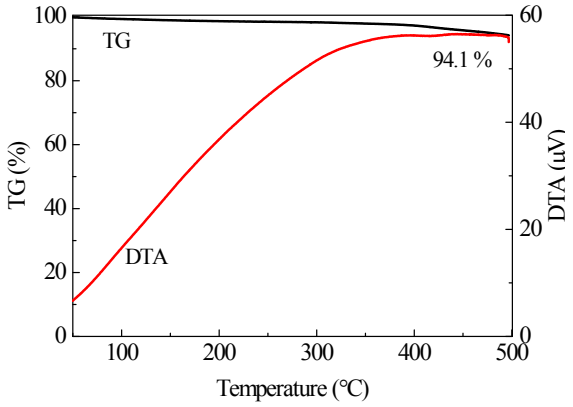

Figure S3. TG-DTA curves of as-prepared bifunctional carbon Ni/NiO nanofiber catalyst (under N_2 with 10 °C/min).

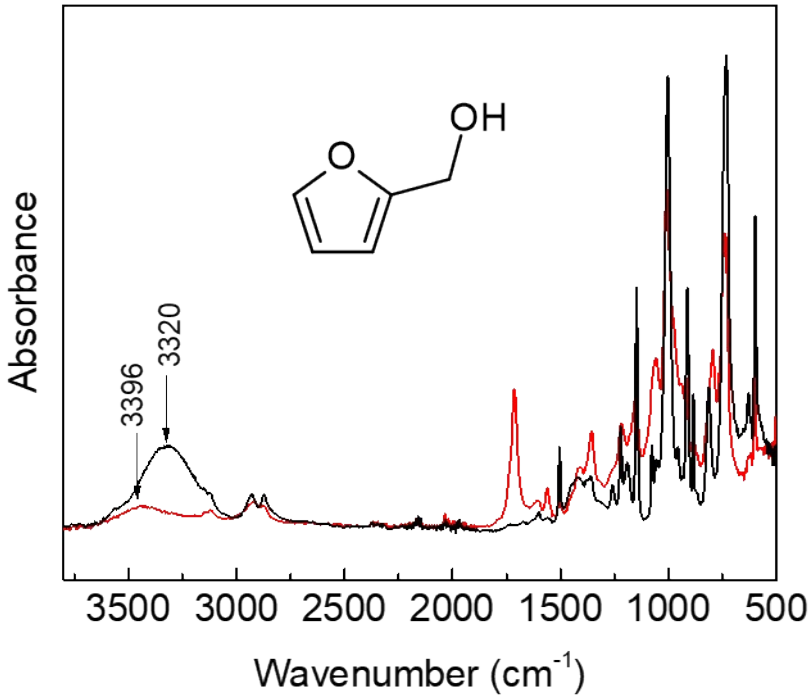

Figure S4. ATR-IR spectra of (black line) furfuryl alcohol and (red line) furfuryl alcohol-Ni/NiO nanofiber mixture system.

Table S1. Adsorption capacity (Q) of sulfonated carbon without amino groups (S-FC) and Ni/NiO nanofiber catalyst for furfuryl alcohol at 20 ^{o}C.

Samples	Functional groups	Total acidity (mmol/g)	Q (mmol/g)
Amberlyst-15	$-SO_3H$, -OH	4.7	-
S-FC	$-SO_3H$, -OH, -COOH	3.54	0.1
Ni/NiO nanofiber	$-SO_3H$, -OH, -COOH, NH_2	5.5	2.5

Conditions: 0.1 g FAL, 5 mL ethanol, 0.05 g adsorbent

Analysis

A gas chromatograph (GC-Shimadzu-14C, Capillary column, Rtx-Wax 30 m × 0.53 mm × 1 μm) and a gas chromatograph/mass spectrometer (GC/MS, Agilent 78900 GC/5795 MSD) and a mass selective detector and flame ionization detector (FID) were used to analyze samples for substrate conversion and products yields. The carrier gas was N_2 with a flowrate of 1.0 mL/min and the temperature program was (60 to 230) °C (heating rate, 10 °C/min). Products of 5-HMF yields, 5-EMF yields, and fructose conversion were analyzed with high-performance liquid chromatography (HPLC) equipped with a refractive index detector using HPLC-RI SH 1011 column with an oven temperature of 60 ºC. Mobile phase used in HPLC analyses was sulfuric acid aqueous solution (0.5 mM) at a flow rate of 1 mL/min. All results were replicated at least two times and the reproducibility of product yields was within 3 % standard deviation.

[1]H NMR spectra of sample

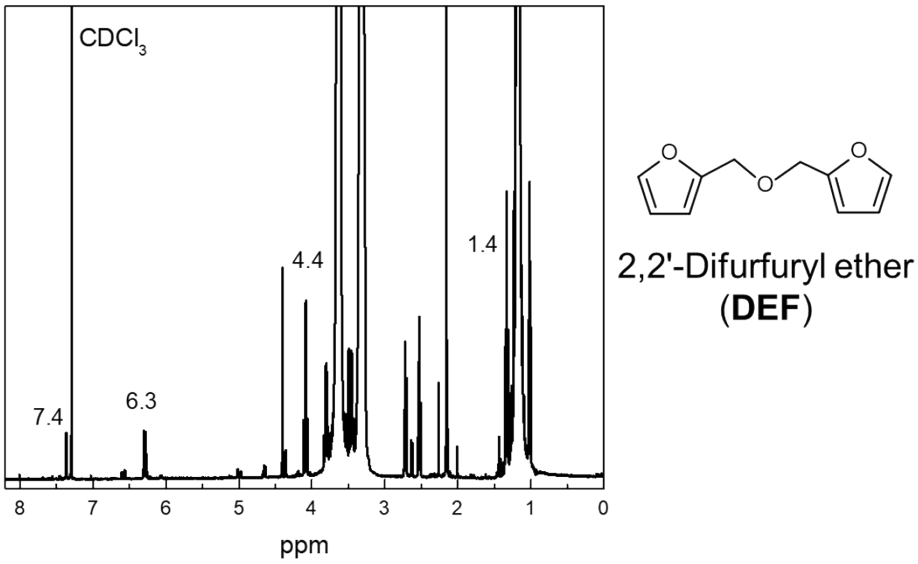

Figure S5. Analysis with [1]H NMR of formed byproducts during the course of one-pot conversion of furfuryl alcohol (FAL) with Ni/NiO bifunctional nanofiber catalyst. Reaction conditions: 0.1 g furfuryl alcohol, 0.05 g catalyst, reaction temperature, 150 ºC, reaction time, 4 h.

GC-MS spectrum results

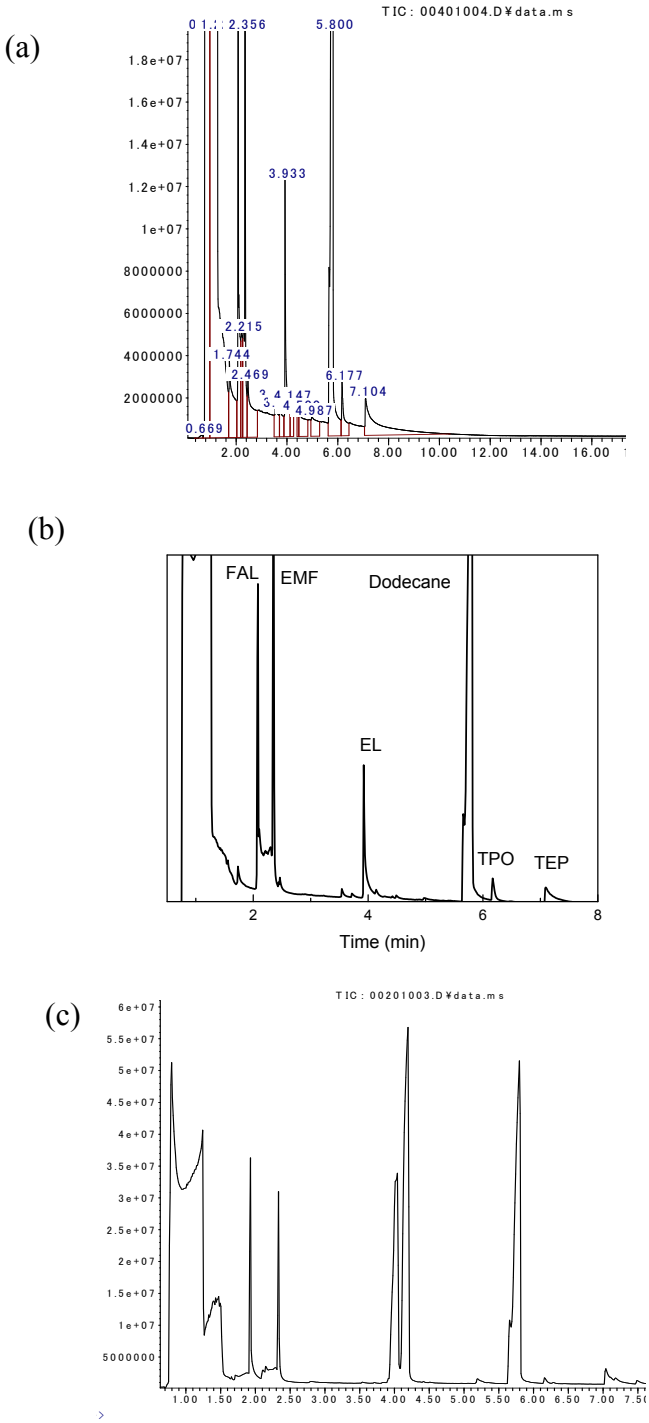

Figure S6. GC-MS spectrum of the intermediate (a) and products formed (b) during the one-pot conversion of furfuryl alcohol (FAL) with Ni/NiO bifunctional nanofiber catalyst 140 ºC (c) one-pot conversion of furfural with Ni/NiO bifunctional nanofiber

catalyst at 150 ºC. Products: ethyl levulinate (EL), 2-(ethoxymethyl)furan (2-EMF), 4,5,5-triethoxypentan-2-one (TEP) and 2,5,5-triethoxypentan-2-one (TPO).

Table S2. Carbon balance calculation for the synthesis of ethyl levulinate from furfural alcohol at different reaction temperatures after 6 h reaction time. (2-(ethoxymethyl)furan (2-EMF), 4,5,5-triethoxypentan-2-one (TEP) and 2,5,5-triethoxpentan-2-one (TPO)).

T	Conv.	Percentage of FAL used for product (%)				
(ºC)	(%)	EL	2-EMF	TPO	TEP	Total
130	-	-	-	-	-	-
140	46.9	67.4	13.6	4.5	1.1	86.6
150	74	70.4	15.2	6.8	1.7	94.1
160	100	52.8	4.3	7.1	3.3	67.5

Reaction conditions are described in Figure 5.

Table S3. Effect of reaction temperature and time on (a) furfural alcohol conversion and (b) ethyl levulinate selectivity for furfural alcohol etherification-hydrolysis catalyzed by as-prepared nanofiber catalyst in ethanol.

Entry	T (°C)	Time (h)	Conv. (%)	EL select. (%)
1	130	10	8	-
2	140	4	35.1	41.9
3		6	46.9	67.4
4		8	68.9	54.7
5		10	73.8	40.4
6	150	2	34.2	63.5
7		4	41.5	70.4
8		8	87	54.1
9[a]		6	100	44
10	160	2	54	45
11		4	72.1	52.3
12		5	88.3	62.6
13		6	100	52.8

Reaction conditions: 0.1 g furfural alcohol, 0.05 g catalyst, 3 mL ethanol. [a]using 0.05 g Amberlyst-15 instead of as-prepared catalyst.

Section 2. Reuse and recycle of catalyst

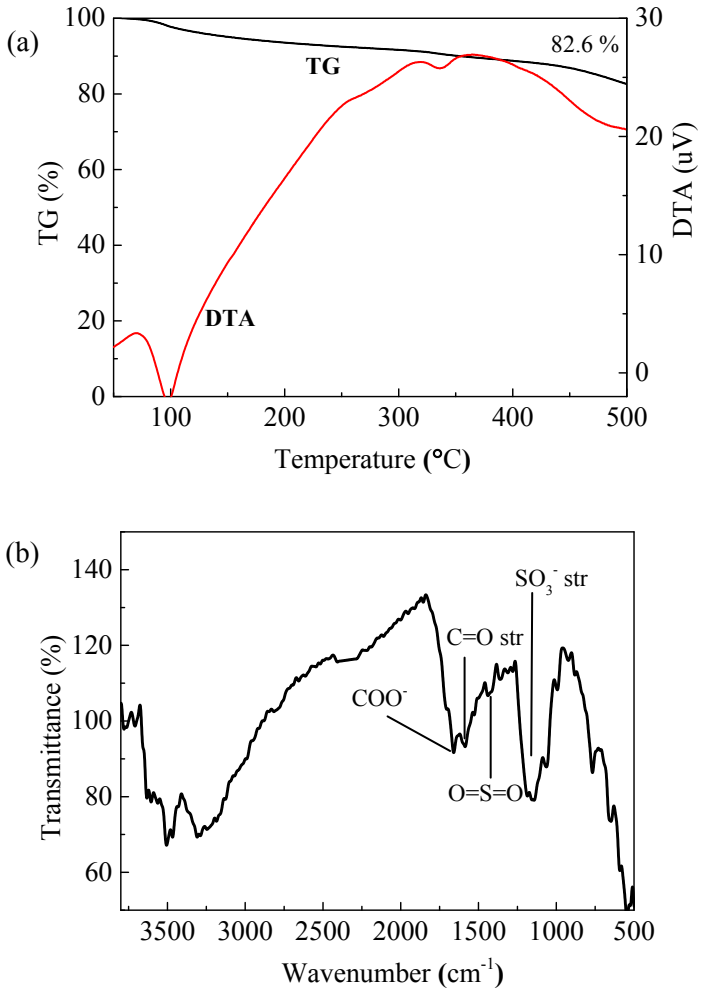

Figure S7. Thermal and spectral analyses of the spent Ni/NiO bifunctional nanofiber catalyst: (a) TG-DTA curve and (b) FT-IR spectra.