Supplementary Data

Direct One-pot Conversion of Monosaccharides into High-yield 2,5-Dimethylfuran over a Multifunctional Pd/Zr-Based Metal–Organic Framework@Sulfonated Graphene Oxide Catalyst

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Experimental Section

Materials

All chemicals were used as received without further purification. Graphite (powder, $< 45 \mu m$, > 99.99%), potassium permanganate (KMnO₄, $\ge 99.0\%$), palladium chloride (PdCl₂, > 99%), sulfuric acid (H₂SO₄, 98%), sodium bicarbonate (NaHCO₃, \geq 99.7%), sodium hydroxide (NaOH, ≥97.0%, pellets), D-Glucose (>99%), 5-(hydroxymethyl)furfural (5-HMF, analytical standard), 5-methylfurfural (5-MFA, analytical standard), 2,5-dimethyltetrahydrofuran (2,5-DMTHF, 96%) were purchased from Sigma Aldrich (USA). Zirconium chloride (ZrCl₄, > 99.5%), sodium chloride (NaCl, > 99%), hydrazine monohydrate (N₂H₄.H₂O, > 98%) as reducing agent of Pd^{2+} to Pd^{0} , D-Fructose (> 98%), 2-furaldehyde (FA, > 98%), and 2,5dimethylfuran (2,5-DMF, > 98%) were purchased from Alfa Aesar (South Korea). Sulfanilic acid ($C_6H_7NO_3S_2 > 99\%$) and 1,4-benzenedicarboxylic acid ($C_8H_6O_4 > 99,0\%$) were purchased from Tokyo Chemical Industry (TCI, South Korea). Hydrogen peroxide (H₂O₂, 30% in water) was purchased from Junsei Chemical (Japan). Distilled and deionized (DDI) water were prepared using an AquaMax Basic 360 water purification system equipped with a 0.22 µm filter (Young Lin Instrument Co., Ltd., South Korea). Sodium nitrate (NaNO₂, 99%), hydrochloric acid (HCl, 35%), N,N-dimethylformamide (C₃H₇NO, 99.9%), tetrahydrofuran (THF, C₄H₈O, 99.5%), and acetone (CH₃COCH₃, 99.8%) were purchased from Daejung Chemical (South Korea).

Catalyst Preparation

Graphene Oxide and Sulfonated Graphene Oxide

Graphene oxide (GO) was prepared by oxidative treatment of graphite according to the modified Hummer's method.¹ The detailed description of the GO preparation is given in our previous papers.²⁻⁴ For the synthesis of sulfonated graphene oxide (SGO), first the diazotization

of sulfanilic acid with NaNO₂ was carried out to produce an aryl-diazonium salt, which was used in the sulfonation step, according to the method described by Verma et al.⁵ Briefly, 5 mmol of sulfanilic acid and 5.2 mmol of NaNO₂ were dissolved in 100 g of DDI water, followed by the addition of 1 N HCl at 0 °C. The produced diazonium salt solution was then added to a suspension of 100 mg of GO (1.0 mg mL⁻¹) in DDI water at 3-5 °C under stirring for 2.5 h. Hereafter, the produced sulfonated GO (SGO) was repeatedly washed and centrifuged 2-3 times with DDI water to remove the excess reactant and impurities, and then dried in vacuum at 70 °C overnight.

Synthesis of UiO-66

The Zr-benzenedicarboxylic acid metal-organic framework, known as UiO-66, was prepared in large scale under acidic conditions.⁶ Briefly, 5 g of ZrCl₄ (21.6 mmol) and 40 mL of 35% HCl were mixed and dissolved with 200 mL of *N*,*N*-dimethylformamide under ultrasonication for 30 min. Then 4.98 g of terephthalic acid (30 mmol) was added to the ZrCl₄ solution and further sonicated with additional 400 mL of N, N-dimethylformamide for the next 30 min. As a result, a clear transparent solution that was homogeneously dissolved in the solvent was obtained. Afterwards, the solution was kept at 80 °C in a convection oven overnight. The white precipitate, as a result of the UiO-66 crystallization, was recovered by vacuum filtration at room temperature, subsequently washed twice with 150 mL of DMF and 150 mL of ethanol to remove the unreacted ligand, and finally vacuum-dried at 70 °C overnight.

Synthesis of Pd/UiO-66@SGO

The Pd/UiO-66@SGO catalyst was prepared by a consecutive procedure of Pd-loading on UiO-66 followed by the addition of ethanol dispersed SGO. Firstly, the palladium was loaded onto UiO-66 by salt impregnation, followed by reduction of Pd²⁺ to Pd⁰ using hydrazine monohydrate.⁷ For the preparation of 2.4Pd/UiO-66@SGO, 41.4 mg of PdCl₂ was dissolved completely in 25 mL of ethanol. Then 488 mg of vacuum-dried UiO-66 was added to the

solution, which was continuously stirred for 12 h to ensure the homogeneous distribution of the Pd²⁺ ions in solution until a light brown milky solution was formed, which is indicative of a uniform dispersion of Pd²⁺. Subsequently, the reduction of Pd²⁺ was carried out by adding 250 μ L of hydrazine monohydrate to the solution. The color of solution changed to light grey shortly afterwards. The mixture was then stirred for 2 h at room temperature. Meanwhile, 488 mg of SGO was dispersed in 25 mL ethanol for 1 h, and this solution was then added to the Pd/UiO-66 solution and stirred for further 4 h. The free Pd nanoparticles in the solution phase that were not attached to UiO-66, were deposited on the SGO surface. Finally, the catalyst was washed with ethanol, filtered, and dried overnight in a vacuum oven at 70 °C. For the preparation of 4.8Pd/UiO-66@SGO, 83.3 mg of PdCl₂ was dissolved completely in 25 mL of ethanol, and then the same procedure used for the preparation of 2.4Pd/UiO-66@SGO was followed.

Characterization of the catalysts and product analysis

X-ray diffraction (XRD) patterns were collected at a scanning range of 5–80° (scanning speed of 0.02° per second) with Cu-K α (λ = 1.5418 Å) Ni-filtered radiation at 40 kV and 50 mA using a D/Max-2500V/PC Rigaku X-ray diffractometer (Japan). The morphology of the catalysts was observed by field-emission scanning electron microscopy (FE-SEM, Hitachi S-4100, Japan) and high-resolution transmission electron microscopy (HR-TEM, Tecnai G2 FEI Co. Ltd., USA). The textural properties of the catalysts were measured by N₂ adsorption–desorption at -196 °C using a Belsorp-mini II apparatus (BEL Inc., Japan). The specific surface area was measured according to the Brunauer, Emmett, and Teller (BET) method. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was employed to measure the amount of Pd loaded on the catalysts. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5000 Versa Probe (ULVAC-PHI Inc., Kanagawa, Japan) spectrometer. The contents of carbon, hydrogen, nitrogen, and sulfur elements in the catalysts were analyzed using an Elementar Vario EL CUBE elemental analyzer (Germany). The temperature-programmed desorption of ammonia (NH₃-TPD) was conducted on an Autochem II chemisorption analyzer (Micromeritics, 2920) to determine the acidity of the catalysts. Prior to NH₃-TPD, the samples were subjected to heat-treatment at 250 °C for 3 h under flowing He at a rate of 30 mL min⁻¹ and cooled to 100 °C. NH₃ gas was adsorbed using 10% NH₃ in Ar for 1 h. Desorption was conducted by increasing temperature from 100 to 700 °C at a rate of 10 °C min⁻¹ under flowing He at a rate of 30 mL min⁻¹.

The reaction products were qualitatively and quantitatively analyzed using gas chromatography-time of flight mass spectrometry (GC-TOF/MS). An Agilent 7890N GC (Agilent Technologies, USA) and Pegasus high-throughput (HT) TOF-MS system (Leco Corporation, USA) were equipped with an auto injector (Agilent 7860N) and middle range polarity, Rxi-5Sil-MS, column (30 m x 0.25 mm x 0.25 µm). Ultrahigh purity helium (99.9999%) was used as carrier gas at a flow rate of 1.0 mL min⁻¹. Typically 1 µL of fresh product solution was injected into the column in a split mode of 25:1. The injector temperature was set at 250 °C, while the transfer line temperature was fixed at 260 °C. The column temperature was programmed to initiate heating starting from 40 °C, held for 2 min, and then increase to 300 °C with a heating rate of 10 °C min⁻¹. The detectable mass range for the MS was set at 35–650 m/z. GC-FID analysis was conducted using agilent 6890N equipped by FID detector and Rxi-5Sil-MS capillary column with dimension of 30 m x 0.25 µm x 0.25 mm ID. Sampling was done by injection volume 1.0 µL, inlet temperature 250 °C, detector temperature 250 °C, and a split ratio 1:10. Initial column temperature was 40 °C (2 min) with a temperature rise of 10 °C min⁻¹ and final temperature was 250 °C. All product yields and selectivity were calculated by an external standard calibration curve for quantitative analysis. For absorption experiments, High-performance liquid chromatography (HPLC, Waters e2695) equipped with equipped with a Waters 2487 UV detector (320 nm) and a 2414 RI detector was used. The

column used in HPLC was Biorad Aminex HPX-87H (300 x 8.7 mm) with using 0.0013N H_2SO_4 as mobile phase.

Acidity Measurements of GO and SGO by acid-base titration^{8,9}

The acid functional groups in the GO and SGO samples were determined by three types of measurements. First, the concentration of the total acidic functional groups including hydroxyl (-OH), carboxylic acid (-COOH), and sulfonic acid (-SO₃H) groups was measured by adding 30 mL of NaOH 0.05 mol L⁻¹ into 0.25 g of GO or SGO (which was designated as C1). Separately, the concentration of -COOH and -SO₃H groups was measured by adding 30 mL of NaHCO₃ 0.05 mol L⁻¹ into 0.25 g of GO or SGO (which was designated as C2). In addition, the concentration of -SO₃H was measured by adding 30 mL of NaCl 0.05 mol L⁻¹ into 0.25 g of GO or SGO (which was designated as C2). In addition, the concentration of -SO₃H was measured by adding 30 mL of NaCl 0.05 mol L⁻¹ into 0.25 g of GO or SGO (which was designated as C3). Each vial was mixed under ultrasonication for 30 min at room temperature and the mixture was separated by centrifugation. Each supernatant was titrated by using a 0.05 mol L⁻¹ NaOH standard solution in the presence of 5% phenolphthalein solution as indicator. The concentration of each type of functional group was calculated by difference. The -SO₃H group concentration was calculated from C3, the -COOH group concentration was calculated from C1 and C2.

Total Acidity Measurement of UiO-66 and UiO-66@SGO by potentiometric acid-base titration¹⁰

Potentiometric titration was conducted using ThermoscientificTM OrionTM Star A211 pH Benchtop Meter which firstly calibrated using pH buffer solution of 4.00, 7.00, and 10.01 with linear regression result of 99.4%. Typically, 60 ml of 0.01 M NaNO₃ was added to separate vials which contains 50 mg of catalyst. The mixture was then stirred for 18 hours to ensure the equilibrium ion-exchange reagent to release the acidic protons from UiO-66 into the aqueous solution. The mixture was then centrifuged to separate the supernatant and solid phase. Before titration, pH of the supernatant was adjusted to 3.00 using 0.1 M HCl. Afterwards supernatant was then titrated with standardized 0.01 M NaOH until pH 10-11 was achieved. The titration curve was plotted to obtain the end point equivalent.

Components adsorption uptake experiments^{11, 12}

In a typical experiment of fructose adsorption, 10 ml of 5% fructose aqueous solution was added into a 30 ml vials, which contained either SGO or UiO@SGO. The mixture was ultrasonicated for 1 h at room temperature. The mixture was then separated by centrifugation and the remaining fructose concentration in the bulk solution phase was analyzed at every 10 min using HPLC. The adsorption selectivity of 2,5-DMF to 2,5-DMTHF was determined in the presence of either 4.8Pd/SGO or 4.8Pd/UiO-66@SGO. Both 2,5-DMF and 2,5-DMTHF were dissolved in THF and then 4.8Pd/UiO-66@SGO or 4.8Pd/SGO was introduced into the solution. The adsorption experiments were carried out at 25 °C under an ultrasonication condition for 60 min. The 2,5-DMF and 2,5-DMTHF concentration after adsorption were analysed using GC-FID. Adsorption selectivity coefficient of 2,5-DMF over 2,5-DMTHF was calculated according to the reference.¹²

Catalyst performance test

All the experiments were performed in a custom-built SUS 316 batch reactor with an inner volume of 140 mL. The reactor was equipped with a mechanically driven agitator, thermocouples, inlet and outlet gas purge lines. Typically, an experimentally desired amount of reactant (fructose, glucose, or 5-HMF), catalyst, and 40 mL of solvent were added to the reactor and the reaction was conducted at various temperatures and times under 1 MPa of H₂. The reactor was tightly sealed and purged with H₂ three times to remove air. After the reaction finished, cold-water quenching was applied to the reactor to stop the reaction. A small amount of liquid sample (\sim 1 mL) was collected for the product yield analysis. The products in the reactor were then collected and the liquid product was separated from the solid residue (if

formed) and the catalyst by filtration. The solid residue and the used catalyst were washed with acetone and methanol and then mixed with 50 mL of DDI water at 40 °C to dissolve the unconverted glucose or fructose. The remaining solid residue and the catalyst were then separated by filtration and dried in a vacuum oven at 105 °C overnight.

The conversion, product yield, and 2,5-DMF selectivity were calculated using the following equations.

 $Conversion (\%) = \frac{weight of reactant - weight of solid residue}{weight of reactant} \times 100\%$ $Product yield (\%mol) = \frac{mol of product}{mol of reactant} \times 100\%$ $2,5 - DMF selectivity (\%) = \frac{mol of 2,5 - DMF}{mol of reactant - mol of unreacted fructose} \times 100\%$

	Entry	Reactant	Catalyst	Solvent	Т (°С)	P _{H2} (MPa)	Time (hour)	Conversion (%)	2,5-DMF yields (%)	Ref	
Conversi on of 5-HMF	1	5-HMF	Pt/UiO-67	Water	90	2.0	2	31	21	Hester et al., 2016 ¹³	
	2	5-HMF	PtCO/HSC	1-butanol	180	1.0	2	100	98	Wang et al, 2014 ¹⁴	
	3	5-HMF	4.8Pd/UiO-66@SGO	THF	180	1.0	3	>99	99.2	This work	
Two-step ⁻ process ^a -	5	Glucose	12-MPA Pd/C, [EMIM]Cl	Acetonitrile	120	0.62	3 1	- 47	0.14	Chidambaram et al, 2010 ¹⁵	
	6	Fructose	H-Zeolite-Y Cu/ZnO/Al ₂ O ₃	GVL/H ₂ O	240	2.0	120	100	40.6	Xiang et al, 2016 ¹⁶	
	7	Fructose	Amberlyst-15 Ru-Sn/ZnO	n-BuOH	240	1.0	100	100	99	Upare et al, 2015 ¹⁷	
	8	Fructose	NaCl/HCl CuRu/C	n-BuOH	220	0.68	10	10	72	Leshkov et al., 2007 ¹⁸	
	9	Fructose	Formic acid Pd/C, H ₂ SO ₄	THF	150	-	17	100	46	Thananatthanachon et al., 2010 ¹⁹	
	10 Corn stover		CrCl ₃ , HCl	DMA- LiCl/[EMIM]Cl	140	-	2	_	9	Binder et al, 2009 ²⁰	
			CuRu/C	1-butanol	220		10	_		-	
One-pot process ^b	11	Fructose	ZnCl ₂ -Pd/C	THF	150	0.8	8	-	22	Saha et al, 2014 ²¹	
	12	Fructose	AlCl ₃ /H ₂ SO ₄ /H ₃ PO ₄ / Ru/C	N,N-DMF	200	1.5	12	>99	66.3	Wei et al, 2016 ²²	
	13	Fructose	4.8Pd/UiO-66@SGO	THF	160	1.0	3	92	70.5	This work	
	14	Glucose	4.8Pd/UiO-66@SGO	THF	160	1.0	3	87	45.3	This work	

Table S1.	Comparison	of conversions	and product y	ields of 2,5-DMF	using 5-HMF	and monosaccharides
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^{*a*}The two-step process involves (a) the dehydration of carbohydrate to 5-HMF, and (2) hydrogenolysis of 5-HMF to 2,5-DMF. ^{*b*}The one-pot process is the direct conversion of carbohydrates (glucose or fructose) into 2,5-DMF.

	Acidity (mmol g ⁻¹))	Acid amount $(\text{mmol}^{NH_3} \text{g}_{\text{cat}}^{-1})^d$			
Sample	-SO ₃ H	-COOH	-OH	Total	Weak-medium ^e	Strong ^f	Total	
GO ^a	0.19	0.59	0.65	1.33	-	-	-	
SGO ^a	1.71	0.35	0.49	1.95	0.35	1.93	2.28	
UiO-66 ^b	-	-	-	1.85	-	-	-	
UiO-66 ^c	-	-	-	1.31	-	-	-	
2.4Pd/UiO-66@SGO ^b	-	-	-	2.27	0.33	2.83	3.16	
4.8Pd/UiO-66@SGO ^b	-	-	-	2.29	0.26	2.95	3.21	

Table S2. Acidity of supports and catalysts.

^{*a*} Direct titration; ^{*b*} Potentiometric titration; ^{*c*}Synthesized using a method in a reference²³; ^{*d*}Calculated using the NH₃-TPD profiles, ^{*e*}150-300 °C, ^{*f*}300-600 °C,



Fig. S1 (a) XRD patterns, (b) TGA profiles, (c) XPS profiles, (d) N_2 adsorption-desorption isotherms, (e) Pore-size distribution, and (f) Raman spectra of the support and the catalysts.



Fig. S2. NH₃-TPD profiles of (a) SGO, (b) 2.4Pd/UiO-66@SGO and (c) 4.8Pd/UiO-66@SGO



Fig. S3 SEM image of UiO-66.



Fig. S4 HR-TEM image of 4.8Pd/UiO-66@SGO.



Fig. S5 4.8Pd/UiO-66@SGO catalyst surface morphology. (a) SEM image, (b) SEM image for the corresponding elemental mapping of (c) carbon, (d) oxygen, (e) palladium, (f) sulfur, and (g) zirconia. (h) EDX data.



Fig. S6 GC-TOF/MS chromatograms of the fructose conversion in various solvents in the absence of a catalyst. Standard reaction conditions: 0.2 g fructose, 40 mL solvent, 200 °C, 3 h, 1 MPa H₂. (a) Methanol, (b) Ethanol, (c) Isopropyl alcohol, and (d) Tetrahydrofuran.

Fig. S7 GC-TOF/MS chromatograms of the fructose conversion control experiments. Standard reaction conditions: 0.2 g fructose, 0.2 g support, 40 mL THF, 200 °C, 3 h, 1 MPa H₂.

Fig. S8. GC-TOF/MS chromatograms of fructose and 5-HMF conversion using Pd@UiO-66/SGO catalysts. Standard reaction conditions: 0.2 g fructose, 0.2 g catalyst, 40 mL THF, 160 °C, 3 h, 1 MPa H2. Catalysts: (a) 2.4Pd/UiO-66@SGO, (b) 4.8Pd/SGO, (c) 4.8Pd/UiO-66@SGO, and (d) 4.8Pd/UiO-66@SGO using 5-HMF feed.

Fig. S9. The PXRD patterns of the synthesized UiO-66 in this study, reference UiO-66 by Cavka et al.,²³ and the theoretical UiO-66.

The synthesized UiO-66 with HCl exhibits higher full-width-half medium values and some of the peaks associated with theoretical UiO-66 did not appear in the pattern (as indicated by the lines in the figure), suggesting that the crystal lattice of the synthesized UiO-66 have a slightly different arrangement.

Fig. S10 (a) Fructose adsorption on the SGO and the UiO@SGO with adsorption time, and (b) representative HPLC chromatograms of the aqueous fructose solution after the fructose adsorption on the SGO.

Fig. S11 (a) Time-course of 2,5-DMF and 2,5-DMTHF adsorption on (e) 4.8Pd/SGO and (f) 4.8Pd/UiO-66@SGO.

Adsorption selectivity coefficient of 2,5-dimethylfuran over 2,5-dimethyltetrahydrofuran was determined using the equation below, in which q_e and C represent the amount of adsorbed species and initial concentration of the corresponding compounds at the equilibrium point, respectively.

$$S_{2,5-DMF} = \frac{q_{e,2,5-DMF}/C_{2,5-DMF}}{q_{e,2,5-DMTHF}/C_{2,5-DMTHF}}$$

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		Fructose	Glucose		
Name of compounds	R. T. (min)	160 °C, 180 min,	180 °C, 180 min,		
		1 MPa	1 MPa		
Furans					
2-Methyltetrahydrofuran	02:47.3	5.3	5.6		
3-Methyltetrahydrofuran	03:04.7	0.2	0.4		
Tetrahydro-2,5-dimethylfuran	03:07.1	n.d	0.9		
2,5-Dimethyl furan (2.5-DMF)	03:11.1	75.2	51.5		
Tetrahydrofuran-2-ol	04:17.8	0.1	0.2		
Furfural (FA)	05:12.8	0.3	0.6		
Furan-2-methanol	05:35.6	0.3	0.5		
5-Methyltetrahydrofuran-2-methanol	06:37.5	0.8	0.8		
2-(1-hydroxy-1-methyl-2-oxopropyl)-2,5-	07.147	2.0	2.4		
dimethyl-3(2H)-Furanone	0/:14./	2.9	2.4		
5-Methylfuran-2-carboxaldehyde (5-MFA)	07:20.5	6.4	21.3		
Furyl hydroxymethyl ketone	09:33.8	0.1	n.d.		
5-Hydroxymethylfurfural (5-HMF)	11:44.1	0.2	8.3		
Ketones/Lactones					
1-Hydroxypropan-2-one	02:41.6	0.6	0.5		
Acetoin	03:13.2	0.8	1.1		
2-Methylcyclopentanone	05:22.7	0.3	0.3		
2-Methyl-2-Cyclopenten-1-one	05:51.6	0.4	n.d.		
Butyrolactone	06:35.2	3.2	2.4		
Hexane-2,5-dione	06:52.4	0.8	1.1		
3-Methylcyclopentane-1,2-dione	08:34.9	0.5	n.d.		
3-Methylcyclopentane-1,2-dione	08:35.1	0.3	0.4		
2,2-Dimethyl-3-heptanone	08:55.4	0.3	0.8		
Alcohols					
Propylene glycol	03:38.8	0.6	0.8		
1,6-Heptadien-4-ol	06:41.3	0.3	0.1		
Cyclopropyl methyl carbinol	09:06.6	0.1	n.d.		
Monosaccharide					
D-Allose	15:17.3	n.d.	0.2		
1,6-Anhydro-á-D-galactofuranose	16:30.0	n.d.	0.3		

Table S4. The chemical composition (area%) of monosaccharides conversion. Reaction conditions: 0.2 g feed, 0.2 g 2.4Pd/UiO-66@SGO, 40 mL THF, 180 °C, 1 MPa H₂.

Fig. S12. Arrhenius plots of (a) fructose and (b) glucose conversion.

Simple kinetic study follows a first-order reaction based on the feed conversion.

$$\frac{dC_{Fructose}}{dt} = -kC_{fructose} \Rightarrow C_{Fructose(t)} = C_{fructose,(0)}e^{-kt} \Rightarrow \frac{C_{Fructose(t)}}{C_{fructose,(0)}} = e^{-kt}$$

$$\frac{C_{Fructose(t)}}{C_{fructose,(0)}} = 1 - X_{Fructose} \Rightarrow 1 - X_{Fructose} = e^{-kt} \Rightarrow -\ln(1 - X_{Fructose}) = kt$$

$$k = A\exp\left(-\frac{E_a}{R.T}\right) \Rightarrow \qquad \ln k = -\frac{E_a 1}{RT} + \ln A$$

Name of compounds	R. T. (min)	Fructose	Glucose	
Furan				
5-Hydroxymethylfurfural (5-HMF)	11:44.1	53.1	28.8	
Monosaccharide				
D-Mannofuranose	14:41.9	4.8	5.3	
D-Allose	15:17.3	11.5	6.8	
D-Fucose	17:51.6	1.4	n.d.	
1,6-anhydro-α-D-glucofuranose	13.10.8	20.8	15.3	
1,6-anhydro-α-D-glucopyranose (levoglucosan)	15:15.1	n.d	38.6	
1,6-anhydro-α-D-galactofuranose	16:30.0	8.4	5.2	

Table S5. The chemical composition (area%) of monosaccharides conversion. Reaction conditions: 0.2 g feed, 0.2 g 2.4Pd/UiO-66@SGO, 40 mL THF, 180 °C, 1 MPa H₂ for 10 min.

Fig. S13 GC-TOFMS chromatograms of the products from the glucose and fructose conversion. Standard reaction conditions: 0.2 g feed, 0.2 g 2.4Pd/UiO-66@SGO, 40 mL THF. (a) Fructose, 180 °C; (b) fructose, 200 °C; (c) glucose, 200 °C.

Fig. S14 Characterization of the fresh and spent 4.8Pd/UiO-66@SGO catalyst after five cycles of the reusability test; (a) XRD patterns, (b) N₂ adsorption-desorption isotherms, and (c) Pore diameter distribution.

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Sample	Pd (wt%) ^{a}	Element analysis (wt%) ^b				Molar composition		
		С	Н	0	S	C/O	C/H	S/C
GO	-	48.7	3.4	46.7	0.6	1.4	1.2	0.005
SGO	-	72.8	4.6	16.4	6.2	5.9	1.3	0.085
2.4Pd/UiO66@SGO ^c	2.4	50.2	7.7	37.5	4.6	1.8	0.5	0.092
4.8Pd/UiO66@SGO ^c	4.8	53.5	6.8	35.3	4.4	2.0	0.6	0.082
4.8Pd/UiO66@SGO ^{<i>d</i>}	4.3	55.3	7.8	32.6	4.3	2.3	0.6	0.078

Table S6. Elemental contents of GO, SGO, and the Pd@UiO66/SGO catalysts

^{*a*} Measured by ICP-OES; ^{*b*} measured by elemental analysis; ^{*c*} fresh catalyst; ^{*d*} spent catalyst after fructose conversion at 160 °C for 3 h, under 10 bar of H_2 .

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