Electrocatalytic hydrogenation of the formyl group and heteroaromatic ring in furfural on activated carbon cloth-supported ruthenium

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Electronic Supplementary Information (ESI)

Materials

Furfural (99%; Sigma-Adrich, St. Louis, MO/99%; Thermo Fisher Scientific, NJ), furfuryl alcohol (98%; Acros Organics, NJ/98%; Thermo Fisher Scientific, NJ), (±)-tetrahydrofurfuryl alcohol (98%; BeanTown Chemical, Hudson, NH), 2-furoic acid (98%; Sigma-Aldrich, St. Louis, MO), tetrahydro-2-furoic acid (98%; Acros Organics, NJ), δ-valerolactone (AA Blocks, San Diego, CA), 2-methylfuran (99%; Thermo Fisher Scientific, NJ), 2-methyltetrahydrofuran (99%; BeanTown Chemical, Hudson, NH), furoin (95%; AA Blocks, San Diego, CA) phosphoric acid (85%; Jade Scientific, MI), hydrochloric acid solution (Macron Fine Chemicals, Center Valley, PA), propan-2-ol (99.5%; VWR Chemicals, Radnor, PA/99.5%; Sigma-Aldrich, St. Louis, MO), ethanol (200 proof; Koptec, Decon Labs, King of Prussia, PA), ammonium hydroxide solution (28.0-30.0% NH_3 basis; Sigma-Aldrich, St. Louis, MO), dichloromethane (99.9%; Fisher Chemical, Fair Lawn, NJ/99.5%; Sigma-Aldrich, St. Louis, MO), ammonium chloride (99.5%; EMD Chemicals), sodium chloride (Macron Fine Chemicals, Center Valley, PA), sodium borohydride (99%; Acros Organics, NJ) and hexaammineruthenium (III) chloride (99%; Strem Chemicals, Newburyport, MA) were used as received without further purification. Deionized (DI) water from a NANOpure ultrapure water system was used for preparing aqueous solutions.
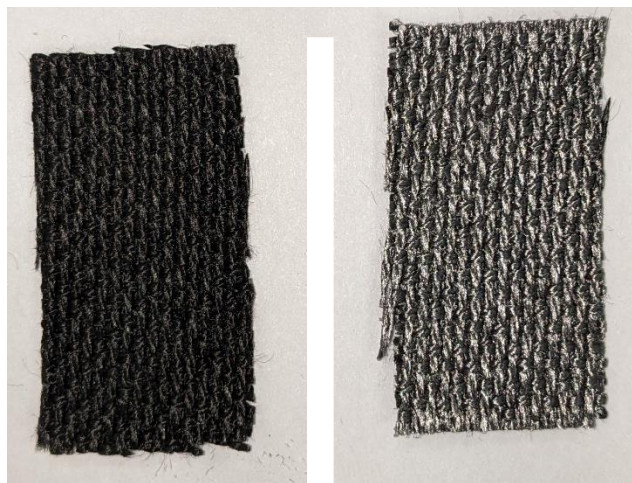
Ru/ACC Electrocatalyst

Fig. S1: Washed and dried ACC (left) and Ru/ACC (right). Note the silver-grey deposition of Ru on the ACC support by electrochemical reduction.
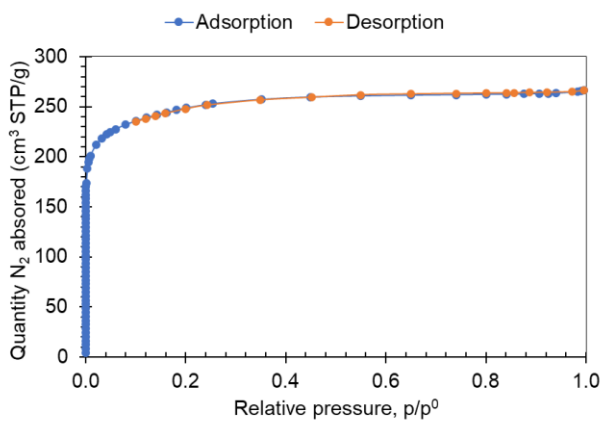

Fig. S2: Nitrogen physisorption isotherms for Ru/ACC at 77 K.
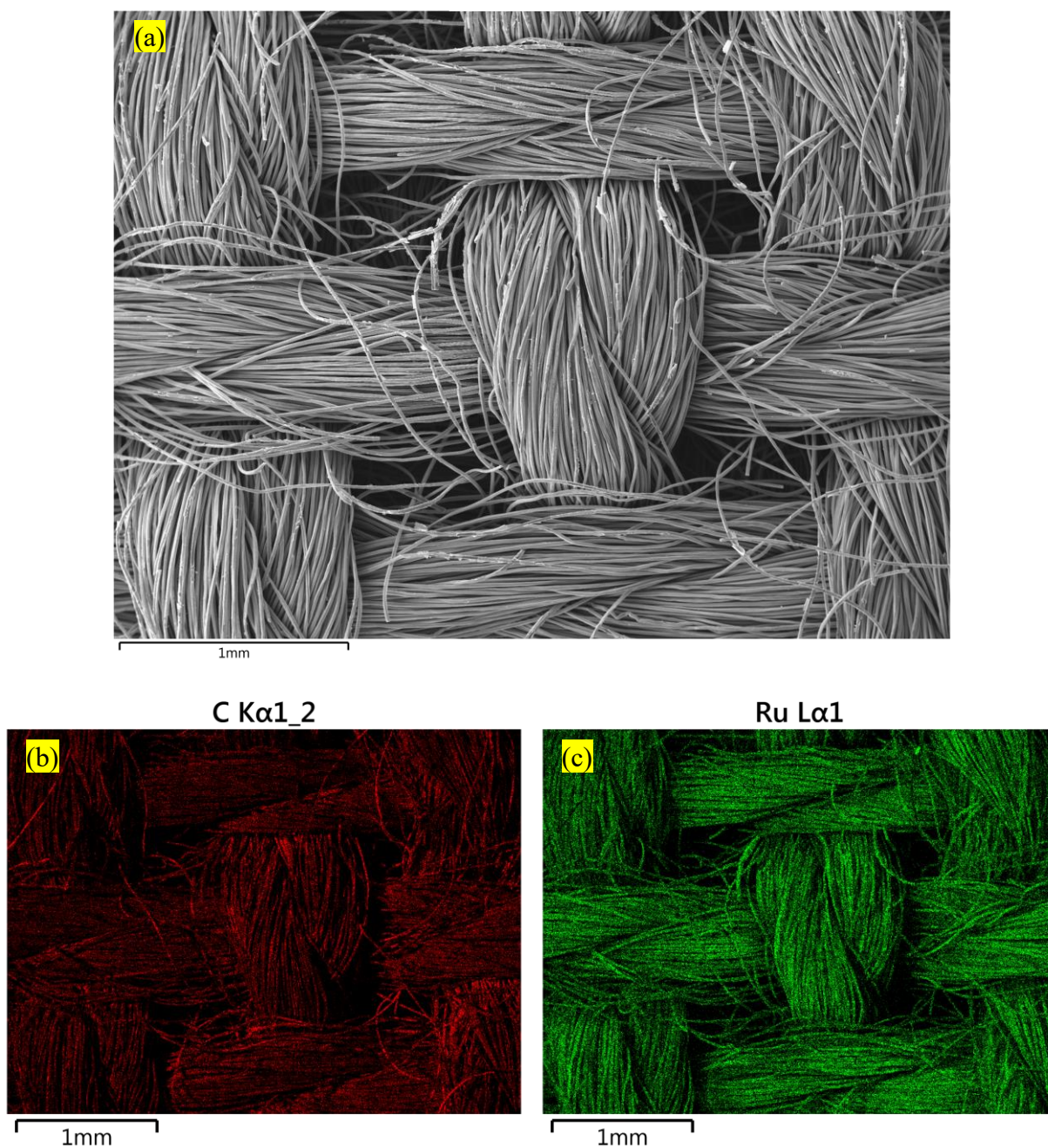
C Kα1_2

Ru Lα1

Fig. S3: (a) SEM image of Ru/ACC and elemental maps of (b) C and (c) Ru collected by EDS. Note the uniform dispersion of Ru on the activated carbon cloth fibers.
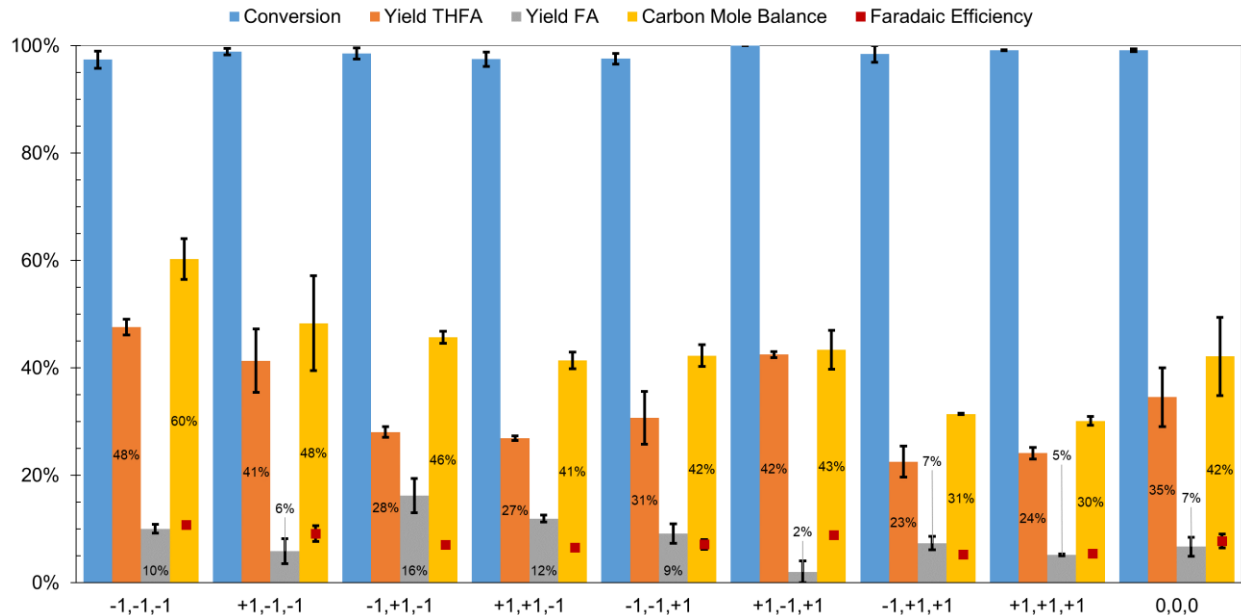
Analysis of Factorial Experiment Design

Fig. S4: ECH of 0.02 M furfural on Ru/ACC using 100 mA current for 2 h. Summary of results for factorial design experiments. The reported faradaic efficiencies are computed with respect to the formation of FA and THFA. Error bars represent standard errors. The x-axis labels follow the A,B,C format, refer to Table 1 for a summary of coded experimental conditions.

Table S1: ANOVA for THFA yield from ECH of furfural (catholyte solution propan-2-ol content [A], catholyte solution acid content [B], and temperature [C]). The main effect B is highly significant at a 95% confidence level as indicated by the small P-value (denoted by *** in the table). Briefly, the ANOVA test procedure involves partitioning the total sum of squares into sum of squares due to A, B, C, AB, AC, BC, ABC, purely quadratic curvature, and error. Each sum of squares divided by its degrees of freedom gives the mean square. The ratio of mean square to error mean square gives the F-value (and P-value). A P-value < 0.05 (95% confidence level) implies that the main effect/interaction/purely quadratic curvature is significant.

Source of Variation	Degrees of Freedom	Sum of Squares	Mean Square	F-Value	P-Value
Model	8	1249.0	156.1	5.0	0.011
Linear	3	1060.7	353.6	11.3	**0.002**
A	1	7.6	7.6	0.2	0.634
B	1	915.1	915.1	29.1	**0.000***
C	1	138.1	138.1	4.4	0.062
2-Way Interactions	3	120.7	40.2	1.3	0.334

3-Way Interactions	1	60.1	60.1	1.9	0.197
Curvature	1	7.6	7.6	0.2	0.634
Error	10	314.2	31.4		
Total	18	1563.2			

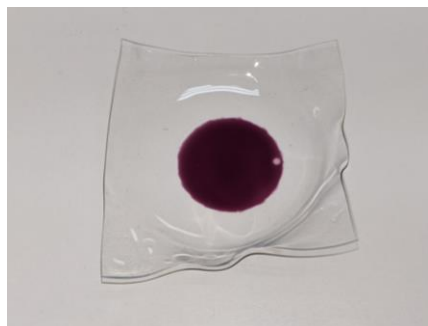Experiments with FA substrate (membrane coloration due to FA)

Fig. S5: Purple coloration of Nafion[TM] membrane in experiments involving FA substrate. Conditions applicable to the membrane in the figure: control experiment (zero current); 0.02 M FA in 0.02 M aqueous HCl solution at 25 °C for 2 h; anolyte: H_3PO_4.

Electrocatalytic Conversion of Furfural to 2-MTHF

The formation of 2-MTHF under relatively severe conditions was investigated. Traces of this product had been observed in the DCM extracts of Ru/ACC in the factorial design experiments. Preliminary data indicated that higher quantities of this product was formed in experiments conducted at higher temperatures (50 °C) and in catholyte solutions with higher acid content (0.16 M HCl). Therefore, experiments were conducted under three different conditions to try and obtain higher yields of the hydrodeoxygenated product. These experiments were conducted in aqueous HCl solutions and involved passage of 100 mA of current for 4 h. The results are summarized in Fig. S6. Nearly complete conversion of furfural, > 95%, was obtained in all three cases. THFA, yield 35%, was the major product in 0.02 M HCl solution at 50 °C while in 0.92 M HCl solution (anolyte solution H_3PO_4 concentration was adjusted to match pH of 0.16 M HCl solution) at 25 °C nearly equal amounts of THFA, yield 15%, and FA, yield 10%, were produced. Only trace quantities of the hydrogenolysis products were obtained in both these experiments. However, experiments conducted in 0.92 M HCl at 50 °C yielded 8% THFA and 4% 2-MTHF. This result suggested that both higher temperatures and highly acidic catholyte solutions were necessary for

the formation of 2-MTHF that agrees with the trends observed in other investigations where the electrocatalytic hydrodeoxygenation of furfural to 2-MF on Cu and Ni cathodes was favored in low pH catholyte solutions.[1-4] The poor mole balance closure in all three experiments may be attributed to the longer run times, high acidity and high temperature conditions that are likely to enhance the rates of the acid promoted side reactions and electron transfer mediated side reactions.
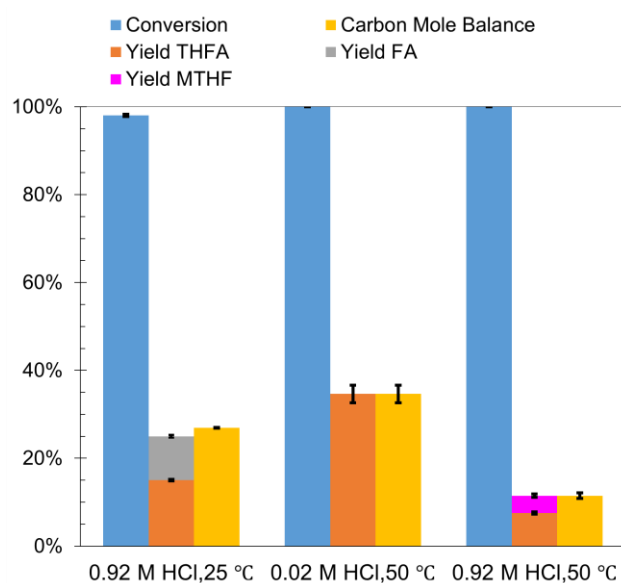

Fig. S6: ECH of furfural on Ru/ACC. Experimental conditions: 0.02 M furfural; 0.02 M or 0.92 M aqueous HCl solution (cathode compartment); 25 °C or 50 °C; 100 mA and 4 h. Error bars represent standard errors.

Electrocatalytic Conversion of Furfural to Saturated Heterocyclic Products

Table S2: A summary of studies on electrocatalytic conversion of furfural to saturated heterocyclic products (THFA and 2-MTHF). The experimental conditions that resulted in the highest yield or selectivity for THFA (or 2-MTHF) are provided.

Study [Reference]	Electrocatalyst	Experimental Conditions	Performance
Green et al. [5]	Pd/C	Mode: continuous Anode compartment fluid: water Cathode compartment fluid: water 1.75 V Temperature: 30 °C	Conversion: 6% Selectivity: THFA: 28% 2-MTHF: 8%

Carl et al. [6]	Pd$_{black}$-5Pd/Al$_2$O$_3$	Mode: continuous Anode compartment fluid: Hydrogen Cathode compartment fluid: Argon 50 mA/cm^2 Temperature: 80 °C	Conversion: decreases from 80% to 20% Selectivity: THFA: ~9% 2-MTHF: ~50%
Delima et al.[7]	Pt/Pd/Pd (served as membrane, electrocatalyst and electrode)	Mode: continuous (water electrolysis); batch (hydrogenation) Electrochemistry compartment fluid: 1 M H$_2$SO$_4$ solution Hydrogenation compartment fluid: n-butanol 225 mA/cm^2	Selectivity: THFA: 98%
Stankovic et al.[8]	Pd/Pd (served as membrane, electrocatalyst and electrode)	Mode: continuous (water electrolysis); batch (hydrogenation) Electrochemistry compartment fluid: 1 M H$_2$SO$_4$ solution Hydrogenation compartment fluid: n-butanol 200, 225 and 300 mA/cm^2	Selectivity: THFA: ~20% 2-MTHF: 76%
Lenk et al.[9]	Pd and Pt (5:1) ink coated on glassy carbon	Mode: batch Anode compartment fluid: 0.5 M H$_2$SO$_4$ solution Cathode compartment fluid: 0.5 M H$_2$SO$_4$ solution 300 mA	Conversion: 51.5% Selectivity: THFA: 15.3%
This study	Ru/ACC	Mode: batch Anode compartment fluid: H$_3$PO$_4$ solution Cathode compartment fluid: 0.02 M HCl solution	Conversion: 97% Yield: THFA: 48%

| | | 60 mA | |
| | | Temperature: 25 °C | |

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