Supplementary Information

Visible light-activated polyphenol-Al³⁺ coordination for ambient and quantitative xylose-to-furfural conversion

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Experimental section

1. Materials

D-xylose (>99%), furfural (>99%), aluminum nitrate nonahydrate $(Al(NO_3)_3 \cdot 9H_2O, >99\%)$, fulvic acid (95%), catechol (99%), pyrogallol (≥99%), benzyl alcohol (≥99%), benzoic acid (99%), 1,2,4-benzenetricarboxylic acid (98%), nitrobenzene (≥99%), benzoin (≥99%), guaiacol (≥98%), 3,5-dinitrosalicylic acid (≥98%), 4-propylphenol (≥99%), 2,4-dinitroaniline (99%), 2-phenylethylamine (98%), and methanol (≥99.9%) were purchased from Shanghai Aladdin Industrial Co., Ltd. Dimethyl sulfoxide (DMSO, ≥99.9%) was purchased from Tianjin Zhiyuan Chemical Reagent Co., Ltd. All the chemical reagents used in this study have not undergone any purification process. Bio-graphene was originated from our team's previous research work.[S1]

2. Catalytic conversion of xylose to furfural

Catalytic furfural synthesis from xylose was carried out in a 15 mL Ace pressure tube. In general, 0.1 M xylose, 0.01 M $Al(NO_3)_3 \cdot 9H_2O$, 2 mL DMSO, 20 mg bio-graphene, and a certain concentration of fulvic acid (FA) ligand (3–11 g/L) were added to the pressure tube, and then nitrogen (30 min) was introduced into the tube and sealed. The pressure tube was further irradiated under simulated sunlight (380–780 nm) and stirred to react for 10–80 min. After the reaction was completed and cooled to room temperature, the reaction mixture was taken out and bio-graphene was separated by filtration. Finally, the reaction solution was diluted 50 times with deionized water using a volumetric method, and the conversion rate of xylose and the yield of furfural were quantified by high-performance liquid chromatography (HPLC).

3. Detection and analysis of products

The concentration of xylose was determined by HPLC (Agilent 1260) with a high Plex H ligand exchange column (300 mm × 7.7 mm × 8 μm). The mobile phase was 5 mM H_2SO_4 (flow rate 0.5 mL/min). The temperature of the refractive index detector (RID) and the chromatographic column was maintained at 50 °C for 2 h of equilibration.

The furfural product was quantitatively analyzed by HPLC (Agilent 11260 equipped with a UV detector). The mobile phase (0.5 mL/ min) was methanol/water (90: 10 v/v) at the wavelength of 280 nm with a Waters C18 column at room temperature. The xylose conversion and furfural yield were calculated as follows:

$$Xylose\ conversion\ （\%）=\left(\frac{Mole\ of\ xylose\ converted}{Mole\ of\ initial\ xylose}\right)\times 100\%$$

$$Furfural\ yield\ （\%）=\left(\frac{Mole\ of\ furfural\ produced}{Mole\ of\ initial\ xylose}\right)\times 100\%$$

4. Equipment

The 300 W Xenon lamp was used as the light source to drive the catalytic synthesis of furfural from xylose. The 600 MHz NMR Bruker Advance spectrometer (Bruker, USA) was used to record the ^{27}Al and ^{1}H NMR spectra of the reaction liquid samples at room temperature. The absorption spectra of liquid samples were collected by UV-Vis spectrometer (TU-1901). The fluorescence emission and excitation spectra of the liquid samples were recorded by a Quanta Master 4 fluorescence spectrometer.

5. Theoretical calculations

The B3LYP density functional method with the D3(BJ) dispersion correction was employed in this work to carry out all the computations. The 6-31G(d) basis set was used for the atoms in geometry optimizations using the PCM model with DMSO as the solvent. Vibrational frequency analyses at the same level of theory were performed on all optimized structures to characterize stationary points as local minima or transition states. Furthermore, intrinsic reaction coordinate (IRC) computations were carried out to confirm that transition states connect to the appropriate reactants and products. The single-point energy calculations were carried out using the 6-311++g(d,p) basis set to provide better energy correction.[S2] All DFT theoretical calculations have been carried out using the Gaussian program package.

6. Supplementary Figures
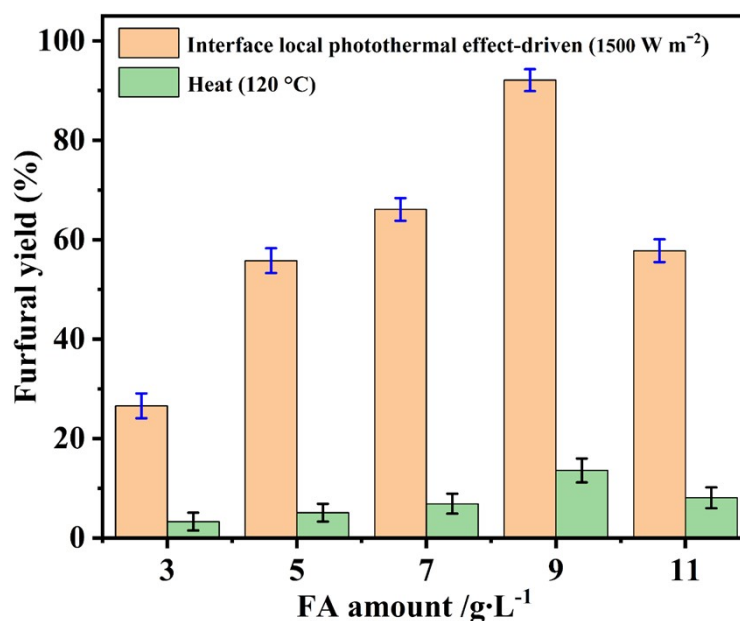
Fig. S1 The effect of the FA amount on the production of furfural from xylose catalyzed by different catalytic systems.
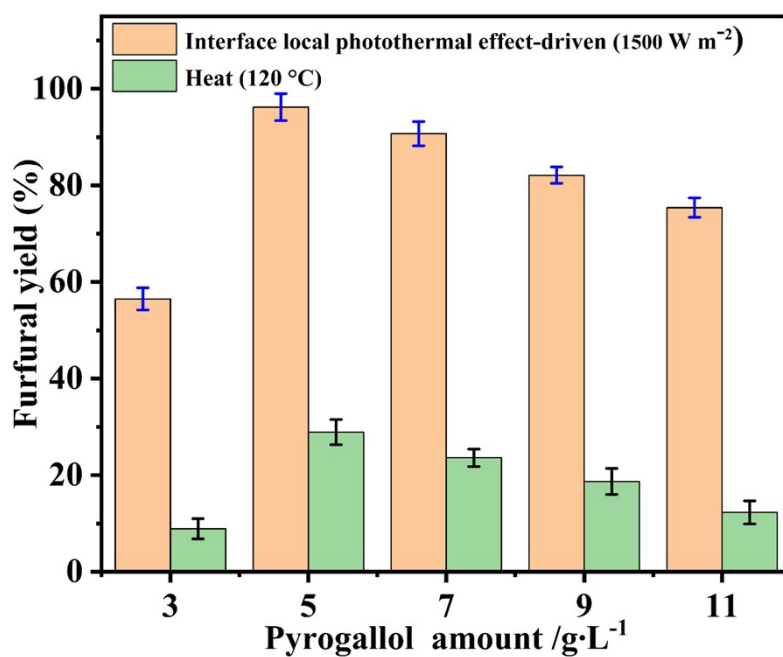
Reaction conditions: 0.1 M xylose, 0.01 M $Al(NO_3)_3 \cdot 9H_2O$, 2 mL DMSO, 20 mg bio-graphene and a certain concentration of fulvic acid ligand, light intensity of 1500 W m^{-2} or 120 °C, and time of 70 min.

Fig. S1 displays that the FA amount had a more obvious impact on the furfural yield for the visible light-enhanced catalytic system compared to the conventional heating process, explicitly disclosing the promotional role of visible light in regulating the distribution of Lewis/Brønsted acid sites for xylose-to-furfural conversion.
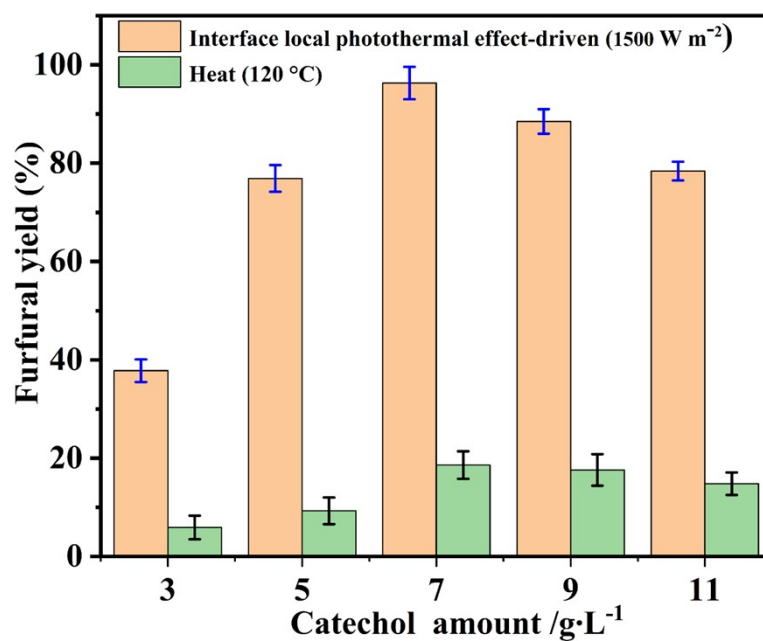
Fig. S2 Effect of catechol ligand dosage on furfural production from xylose. Reaction conditions: 0.1 M xylose, 0.01 M $Al(NO_3)_3 \cdot 9H_2O$, 2 mL DMSO, 20 mg bio-graphene and a certain concentration of catechol ligand, light intensity of 1500 W m^{-2} or 120 °C, and time of 70 min.

Fig. S3 Effect of pyrogallol ligand dosage on furfural production from xylose. Reaction conditions: 0.1 M xylose, 0.01 M Al(NO$_3$)$_3$·9H$_2$O, 2 mL DMSO, 20 mg biographene and a certain concentration of pyrogallol ligand, light intensity of 1500 W m^{-2} or 120 °C, and time of 70 min.
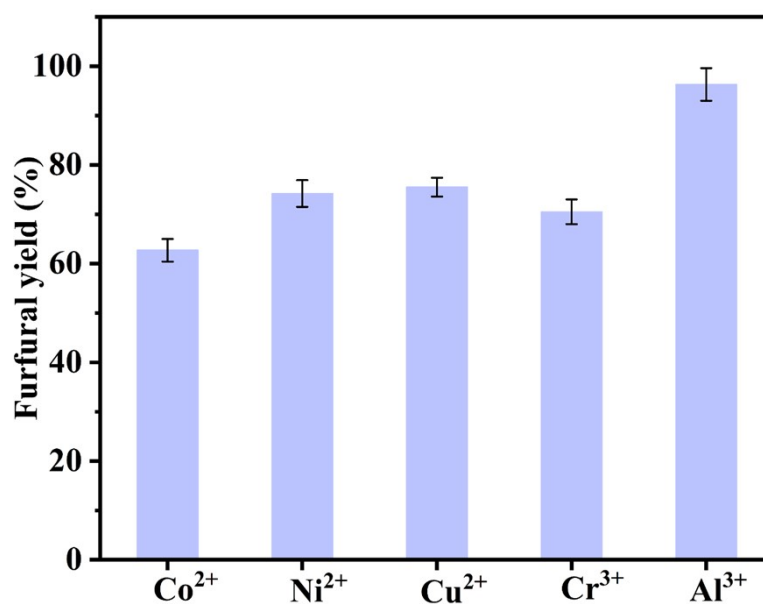
Fig. S4 Activity of different metal nitrate in catalytic conversion of xylose to furfural under interfacial photothermal effect.

Reaction conditions: 0.1 M xylose, 0.01 M metal nitrate, 7 g/L catechol ligand, and 20 mg bio-graphene in 2 mL DMSO at 1500 W m^{-2} light intensity for 70 min

Apart from Al^{3+}, other Lewis acidic metal ions such as Co^{2+}, Ni^{2+}, Cu^{2+}, and Cr^{3+} were also examined for the conversion process, but a relatively high amount of byproducts including lactic acid and formic acid were formed by unselectively photocatalytic redox reactions, leading to the inferior furfural yields (62.7-75.5%).
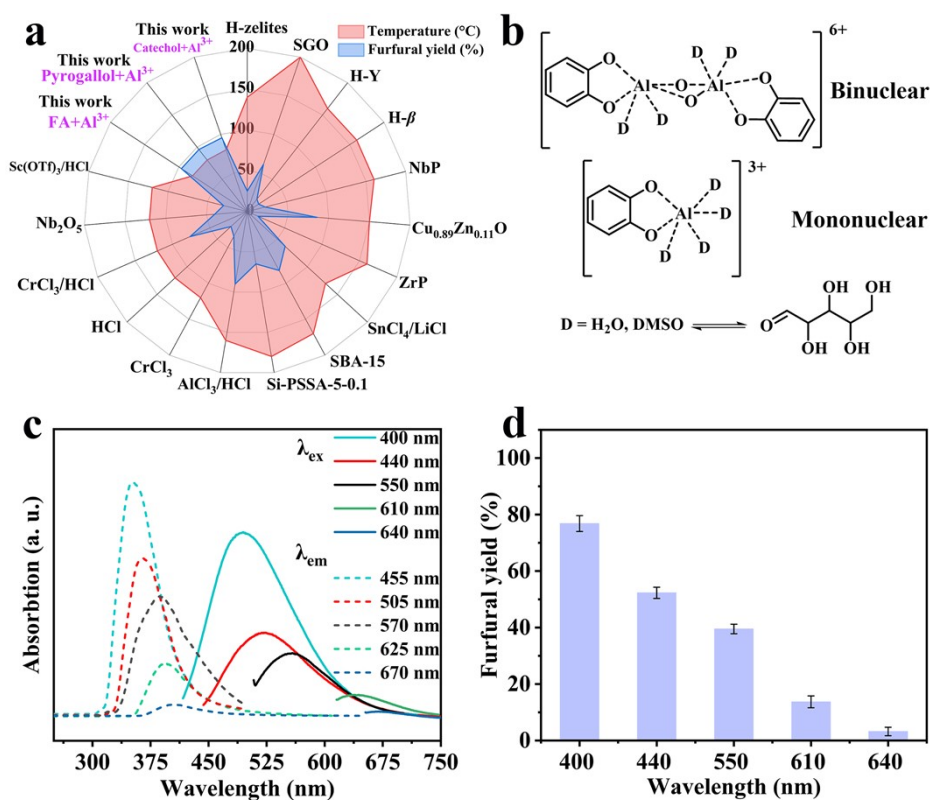
Fig. S5 Activity comparison of different catalysts. (b) Possible mononuclear and binuclear coordination modes of Al^{3+}-centered complexes. (c) Fluorescence spectra of the reaction solution with different excitation/emission wavelengths. (d) The obtained furfural yields at different excitation wavelengths.
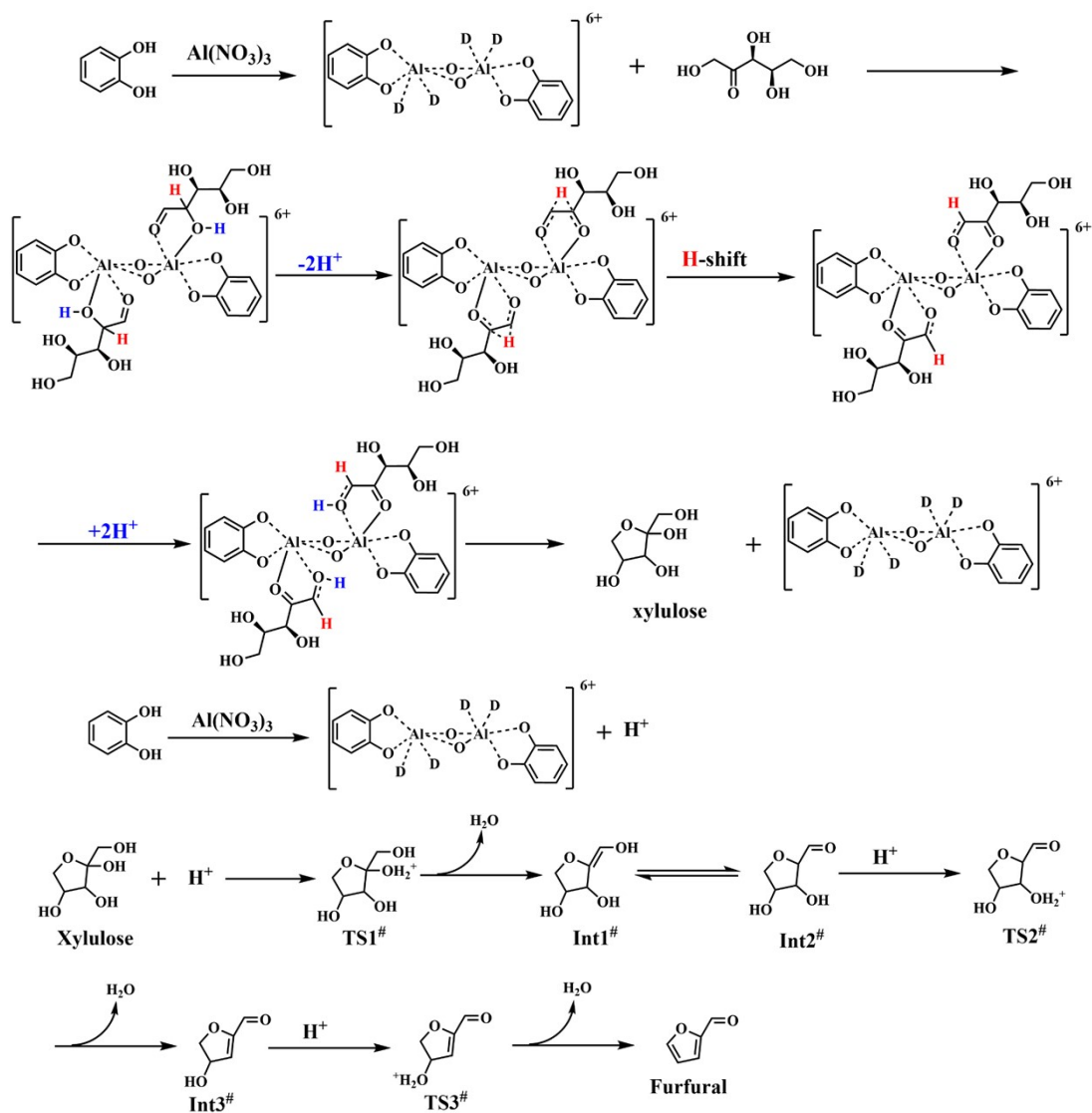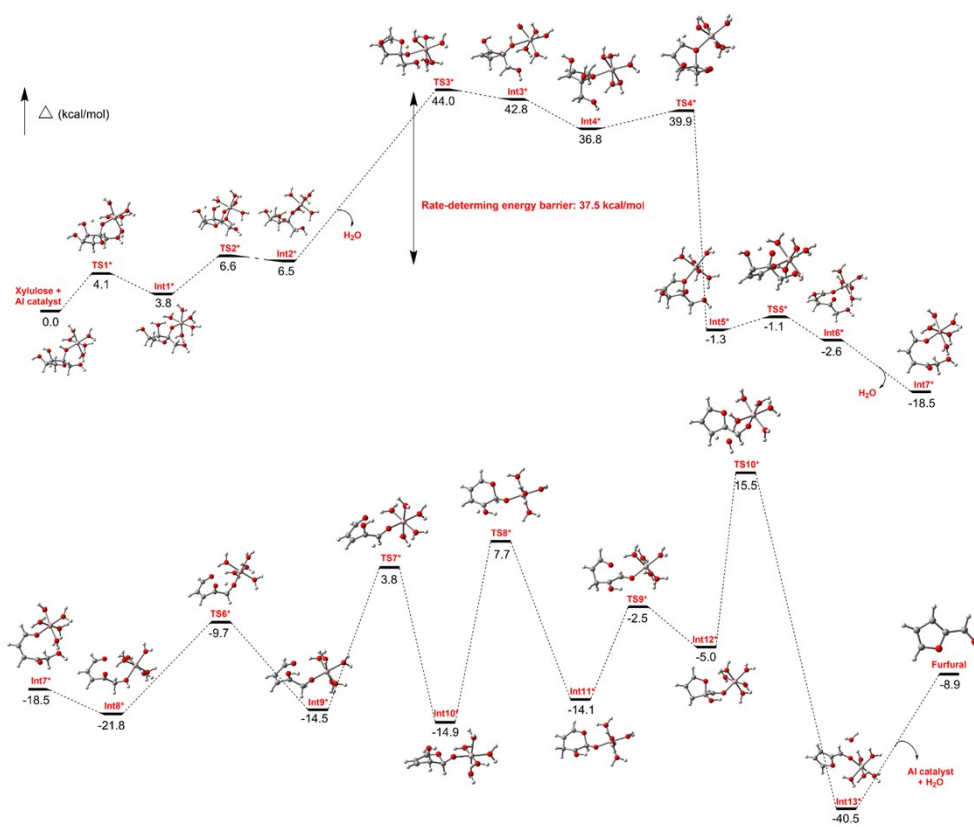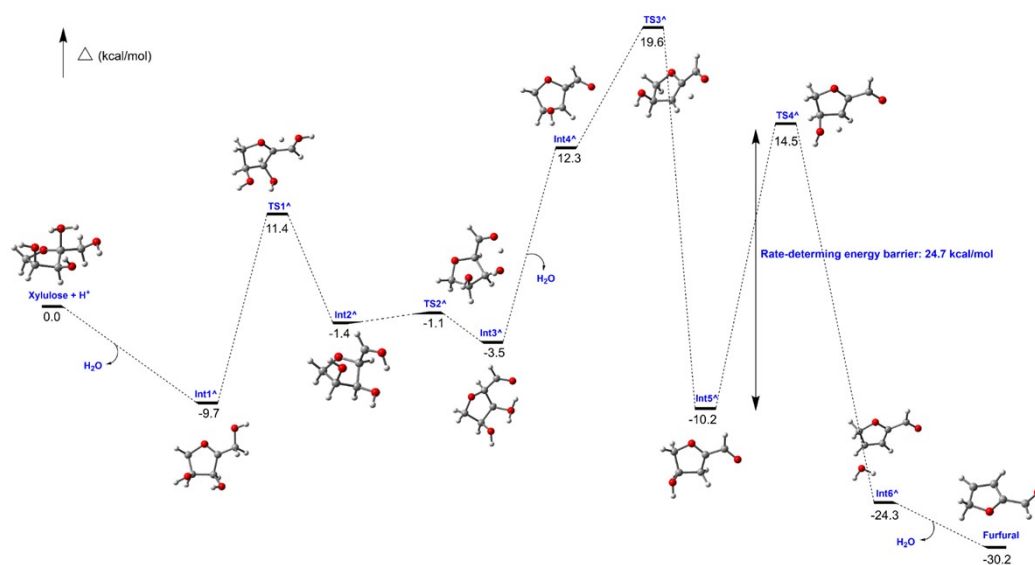
Fig. S6 The proposed mechanism for xylose-to-furfural conversion, involving xylose isomerization and xylulose dehydration catalyzed by Lewis and Brønsted acid, respectively.
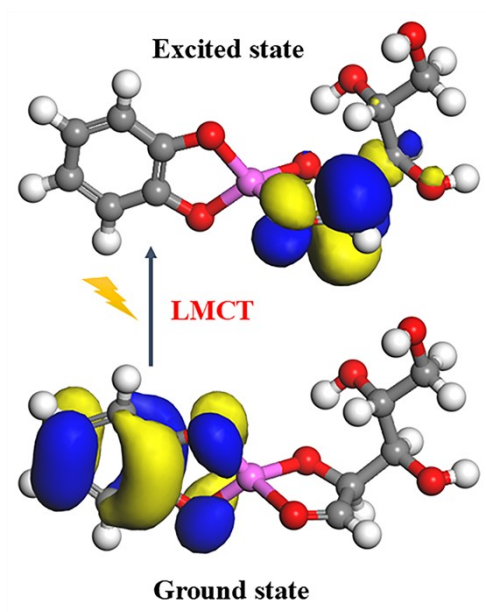
Fig. S7 LMCT effect of mononuclear Al^{3+} complex.

Fig. S8 Reaction free energy diagram of catalytic xylulose dehydration to furfural with the Al³⁺ complex (Lewis acid site).

Fig. S9 Reaction free energy diagram of catalytic xylulose dehydration to furfural with in-situ released Brønsted acid site (H$^+$).

References

S1. J. Huang, T. Liu, K. Wang, Z. Huang, J. Wang, S. L. Rokhum and H. Li, *Environ. Chem. Lett*., 2024, **22**, 1607-1613.

S2. T. Tana, P. Han, A. J. Brock, X. Mao, S. Sarina, E. R. Waclawik, A. Du, S. E. Bottle, and H. Y. Zhu, *Nat. Commun*., 2023, **14**, 4609.