

# **Catalytic conversion of xylose to furfural by *p*-toluenesulfonic acid (*p*TSA) and chlorides: Process optimization and kinetic modeling**

Muhammad Sajid<sup>1,2,3,\*</sup>, Muhammad Rizwan Dilshad<sup>4</sup>, Muhammad Saif Ur Rehman<sup>5</sup>, Dehua

Liu<sup>2</sup>, Xuebing Zhao<sup>2,\*</sup>

<sup>1</sup>*Faculty of Materials and Chemical Engineering, Yibin University, Yibin 644000, Sichuan China;*

<sup>2</sup>*Institute of Applied Chemistry, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China*

<sup>3</sup>*Department of Chemical Engineering, University of Gujrat, Gujrat 50700 Pakistan;*

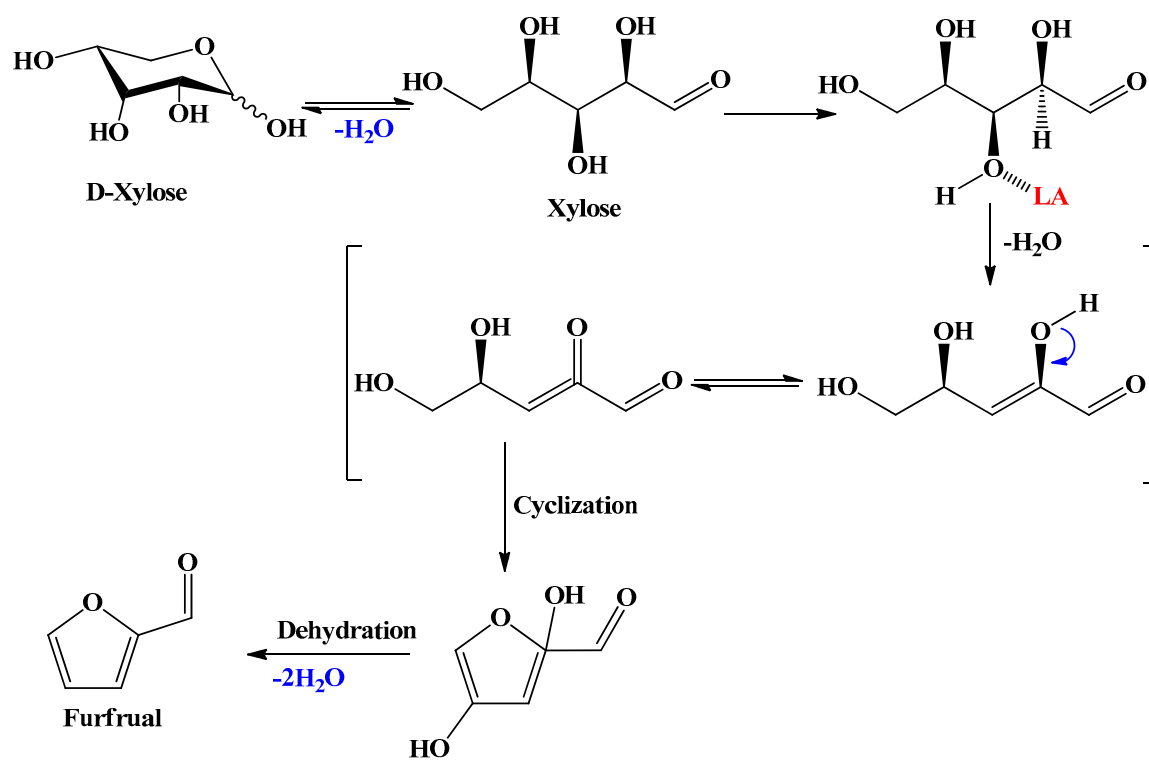
<sup>4</sup>*Institute of Chemical Engineering and Technology, University of the Punjab, Lahore, Pakistan*

<sup>5</sup>*Department of Chemical Engineering, Khwaja Fareed University of Engineering and Information Technology, Abu Dhabi Road, Rahim Yar Khan, Pakistan*

\* Corresponding author: MS engr.sajid80@gmail.com Tel: +86 17810264474 ORCID: 0000-0001-9471-8395;

XZ zhaoxb@mail.tsinghua.edu.cn

**Scheme S1.** Reaction mechanism of acid catalyzed dehydration of xylose to furfural[1,2]



**Table S1.** Xylose transformation into furfural. Reaction conditions: 1.0 M xylose with 1.0 M organic acid in 50 ml water solvent medium heated in an oil bath at 100 °C and stirred at 200 rpm for 8 hours.

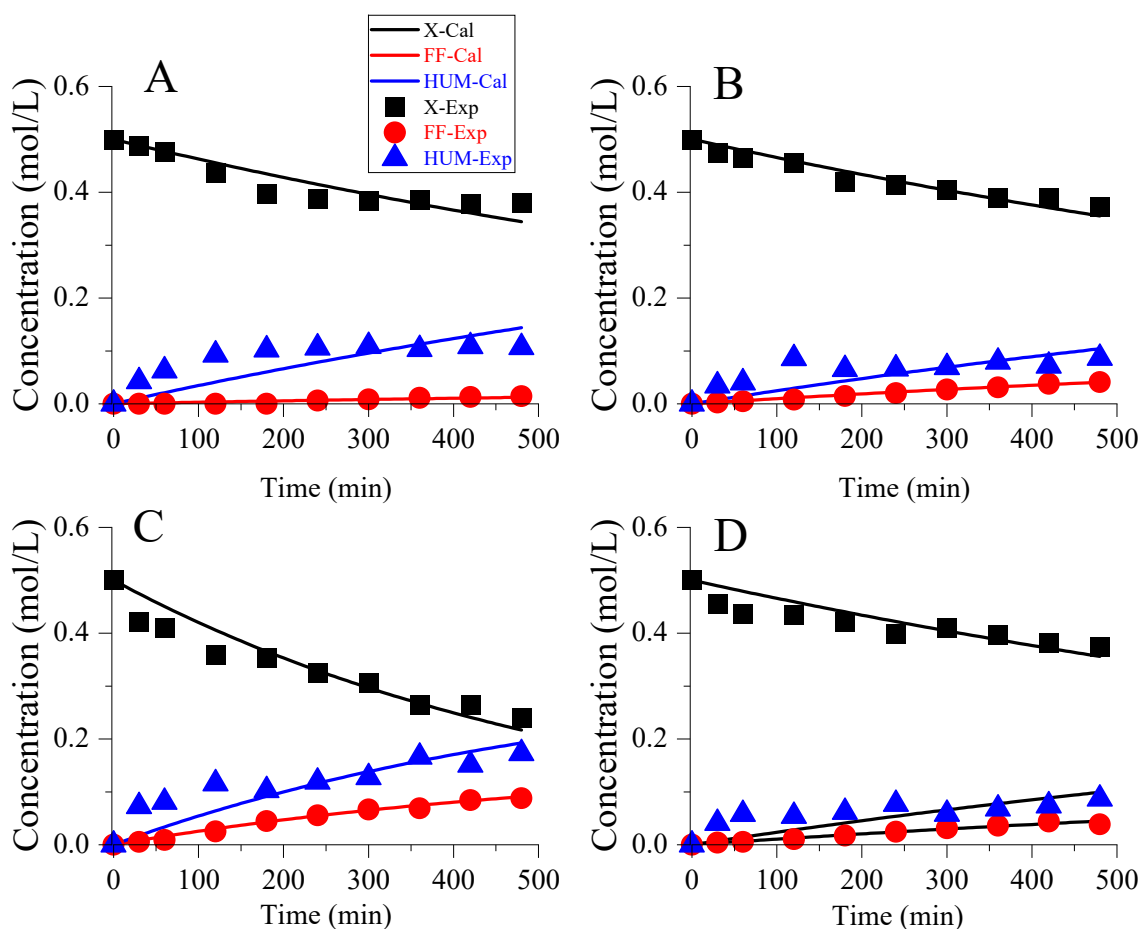
| <b>Organic acid</b> | <b>Xylose conversion<br/>(%)</b> | <b>Furfural yield<br/>(%)</b> |
|---------------------|----------------------------------|-------------------------------|
| <i>p</i> TSA        | 24.2±2.1                         | 2.91                          |
| Oxalic acid         | 20.5±2.0                         | <1                            |
| Maleic acid         | 12.7±1.5                         | <1                            |
| Malonic acid        | 11.7±3.0                         | <1                            |
| Succinic acid       | 6.4±3.5                          | <1                            |

**Table S2.** Fitted kinetic constants of organic acid catalyzed conversion of xylose into furfural in the water medium. Reaction conditions: 0.5 M Xylose with 1.0 M *p*TSA and 0.1 M Lewis acid catalyst in 50 ml water heated in an oil bath at 100 °C with a stirring rate of 200 rpm for 8 hours.

| Lewis acid                           | Rate constant (min <sup>-1</sup> ) |                          |                          | Goodness of Fit (R <sup>2</sup> ) |          | Max yield               |
|--------------------------------------|------------------------------------|--------------------------|--------------------------|-----------------------------------|----------|-------------------------|
|                                      | <i>k</i> <sub>1obs</sub>           | <i>k</i> <sub>2obs</sub> | <i>k</i> <sub>3obs</sub> | Xylose                            | Furfural | <i>Y</i> <sub>max</sub> |
| No Lewis acid<br>(only <i>p</i> TSA) | 6.08×10 <sup>-5</sup>              | 7.17×10 <sup>-4</sup>    | 1.02×10 <sup>-11</sup>   | 0.8505                            | 0.9091   | 2.61±2.5                |
| NH <sub>4</sub> Cl                   | 2.01×10 <sup>-4</sup>              | 5.12×10 <sup>-4</sup>    | 2.22×10 <sup>-14</sup>   | 0.955                             | 0.9926   | 8.3±2.5                 |
| CrCl <sub>3</sub> ·6H <sub>2</sub> O | 5.58×10 <sup>-4</sup>              | 1.18×10 <sup>-3</sup>    | 1.16×10 <sup>-9</sup>    | 0.950                             | 0.9905   | 17.6±2.4                |
| AlCl <sub>3</sub>                    | 2.20×10 <sup>-4</sup>              | 4.88×10 <sup>-4</sup>    | 2.22×10 <sup>-14</sup>   | 0.8476                            | 0.9947   | 8.8±2.2                 |

**Figure S1.** Kinetic plots of *p*TSA-catalyzed conversion of xylose into furfural in the water medium. Reaction conditions: 0.5 M xylose with 1.0 M *p*TSA and 0.1 M Lewis acid catalyst in 50 ml deionized water heated in oil bath at 100 °C for 8 h with a stirring speed of 200 rpm; (A) No Lewis acid addition (only *p*TSA); (B) NH<sub>4</sub>Cl; (C) CrCl<sub>3</sub>·6H<sub>2</sub>O; (D) AlCl<sub>3</sub>. Lines are for model-predicted data, and symbols are for experiment-determined data.

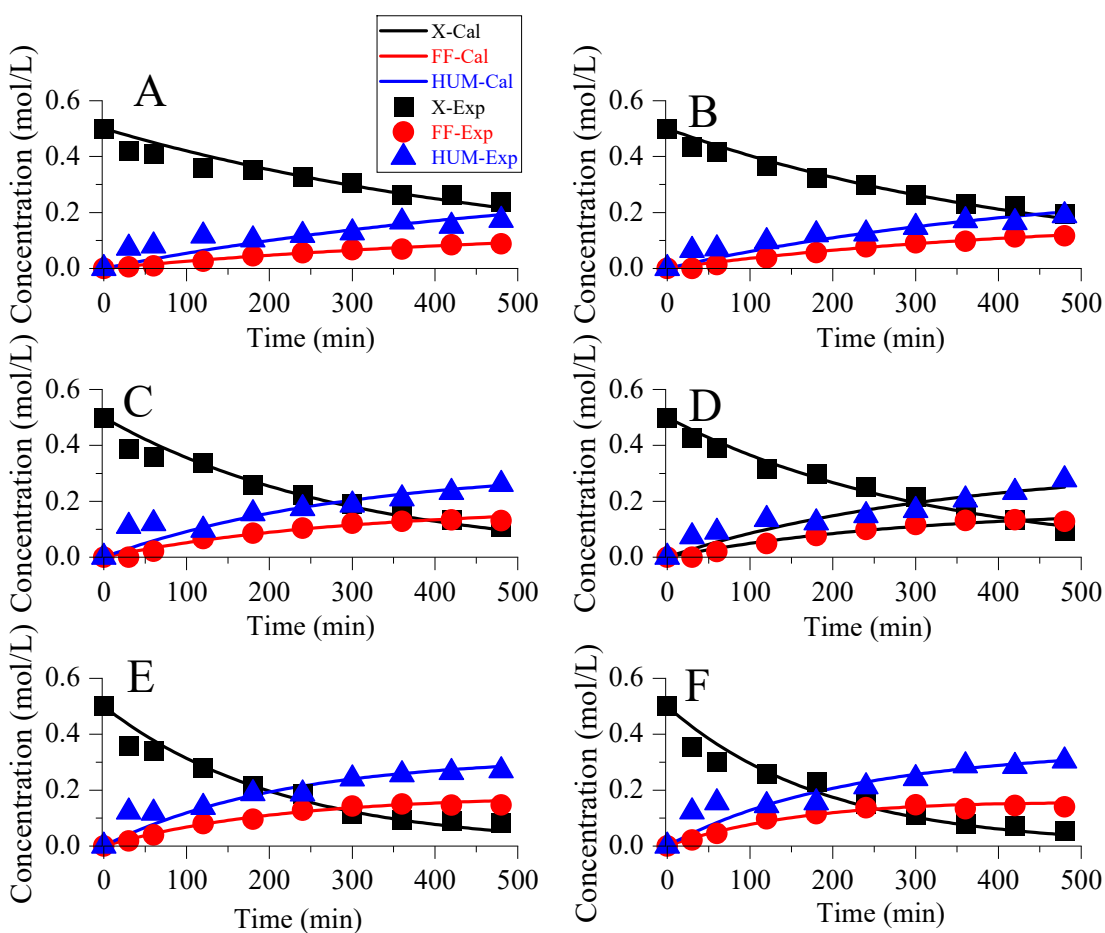
X: xylose; FF: furfural; HUM; humin



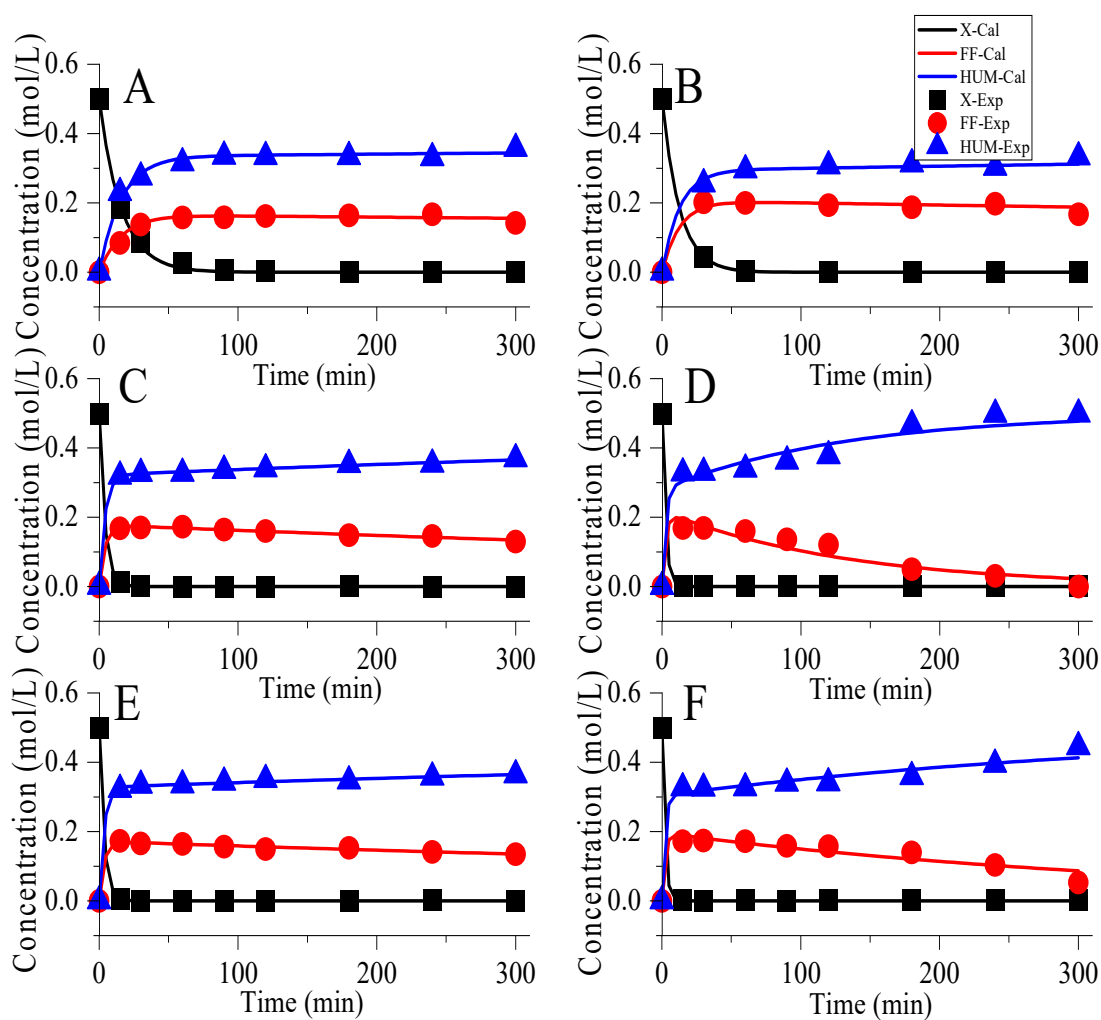
**Table S3.** Fitted kinetic constants of organic acid catalyzed conversion of xylose into furfural in the water medium. Reaction conditions: 0.5 M Xylose with 1.0 M *p*TSA and 0.1 – 0.6 M CrCl<sub>3</sub>.6H<sub>2</sub>O catalyst in 50 ml water at 100 °C with a stirring rate of 200 rpm for 8 h.

| CrCl <sub>3</sub> .6H <sub>2</sub> O<br>Conc. (M) | Rate constant (min <sup>-1</sup> ) |                          |                          | Goodness of Fit<br>(R <sup>2</sup> ) |          | Max<br>yield            |
|---------------------------------------------------|------------------------------------|--------------------------|--------------------------|--------------------------------------|----------|-------------------------|
|                                                   | <i>k</i> <sub>1obs</sub>           | <i>k</i> <sub>2obs</sub> | <i>k</i> <sub>3obs</sub> | Xylose                               | Furfural | <i>Y</i> <sub>max</sub> |
| 0.1                                               | 5.58×10 <sup>-4</sup>              | 1.18×10 <sup>-3</sup>    | 1.16×10 <sup>-9</sup>    | 0.95                                 | 0.9905   | 17.6±1.2                |
| 0.2                                               | 7.98×10 <sup>-4</sup>              | 1.35×10 <sup>-3</sup>    | 2.76×10 <sup>-10</sup>   | 0.9874                               | 0.9922   | 23.4±1.1                |
| 0.3                                               | 1.23×10 <sup>-3</sup>              | 2.17×10 <sup>-3</sup>    | 4.79×10 <sup>-12</sup>   | 0.9755                               | 0.9755   | 26.6±1.5                |
| 0.4                                               | 1.16×10 <sup>-3</sup>              | 1.98×10 <sup>-3</sup>    | 1.14×10 <sup>-4</sup>    | 0.9744                               | 0.981    | 26.8±1.4                |
| 0.5                                               | 1.70×10 <sup>-3</sup>              | 2.97×10 <sup>-3</sup>    | 5.21×10 <sup>-11</sup>   | 0.9744                               | 0.9855   | 30.1±0.9                |
| 0.6                                               | 2.02×10 <sup>-3</sup>              | 3.24×10 <sup>-3</sup>    | 4.28×10 <sup>-4</sup>    | 0.9659                               | 0.9769   | 29.5±1.1                |

**Figure S2.** Kinetic plots of *p*TSA-catalyzed conversion of xylose into furfural in water solvent medium. Reaction conditions: 0.5 M xylose with 1.0 M *p*TSA and 0.1 – 0.6 M CrCl<sub>3</sub>·6H<sub>2</sub>O catalyst in 50 ml water heated in oil bath at 100 °C for 8 h with a stirring speed of 200 rpm; (A) 0.1 M CrCl<sub>3</sub>·6H<sub>2</sub>O; (B) 0.2 M CrCl<sub>3</sub>·6H<sub>2</sub>O; (C) 0.3 M CrCl<sub>3</sub>·6H<sub>2</sub>O; (D) 0.4 M CrCl<sub>3</sub>·6H<sub>2</sub>O; (E) 0.5 M CrCl<sub>3</sub>·6H<sub>2</sub>O; (F) 0.6 M CrCl<sub>3</sub>. Lines are for model-predicted data, and symbols are for experiment-determined data. X: xylose; FF: furfural; HUM; humin

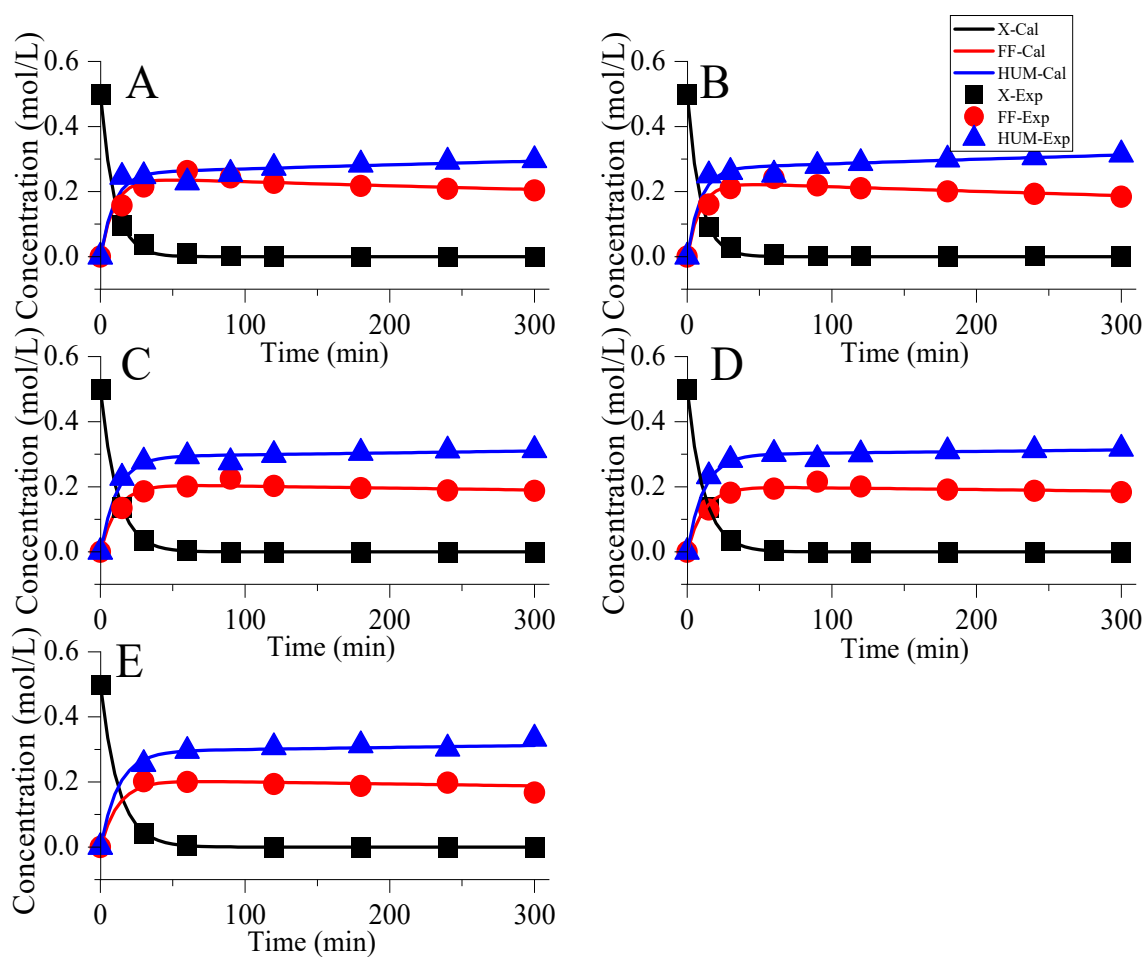


**Figure S3.** Kinetic plots of *p*TSA-catalyzed conversion of xylose into furfural in the DMSO solvent medium. Reaction conditions: 0.5 M xylose with 1.0 M *p*TSA and 0.5 M CrCl<sub>3</sub>·6H<sub>2</sub>O catalysts in 50 ml DMSO heated in oil bath for 5 h with a stirring speed of 200 rpm; the flask was heated at; (A) 110 °C; (B) 120 °C; (C) 130 °C; (D) 140 °C; (E) 150 °C; (F) 160 °C. Lines are for model-predicted data, and symbols are for experiment-determined data. X: xylose; FF: furfural; HUM; humin





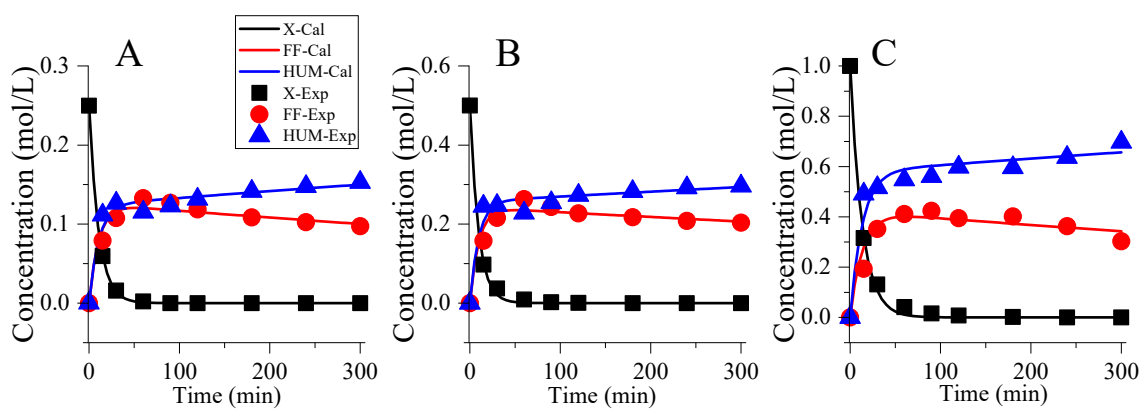
**Figure S4.** Kinetic plots of *p*TSA-catalyzed conversion of xylose into furfural in the DMSO solvent medium. Reaction conditions: 0.5 M xylose with 1.0 M *p*TSA and CrCl<sub>3</sub>·6H<sub>2</sub>O catalysts in 50 ml DMSO heated in oil bath for 5 h with a stirring speed of 200 rpm; the flask was heated in oil bath at 120 °C using different concentrations of CrCl<sub>3</sub>·6H<sub>2</sub>O; (A) 0.1 M; (B) 0.2 M; (C) 0.3 M; (D) 0.4 M; (E) 0.5 M. Lines are for model-predicted data, and symbols are for experiment-determined data. X: xylose; FF: furfural; HUM; humin



**Table S4.** Fitted kinetic constants of organic acid catalyzed conversion of xylose into furfural in DMSO solvent medium. Reaction conditions: 0.25 – 1.0 M Xylose with 1.0 M *p*TSA and 0.1 M CrCl<sub>3</sub>.6H<sub>2</sub>O catalysts in 50 ml DMSO with a stirring rate of 200 rpm heated in an oil bath at 120 °C for 5 h.

| Xylose<br>(M) | Rate constant (min <sup>-1</sup> ) |                          |                          | Goodness of Fit ( <i>R</i> <sup>2</sup> ) |          |        | Max<br>yield            | <i>t</i> <sub>Ymax</sub><br>(h) |
|---------------|------------------------------------|--------------------------|--------------------------|-------------------------------------------|----------|--------|-------------------------|---------------------------------|
|               | <i>k</i> <sub>1obs</sub>           | <i>k</i> <sub>2obs</sub> | <i>k</i> <sub>3obs</sub> | Xylose                                    | Furfural | Humin  | <i>Y</i> <sub>max</sub> |                                 |
| 0.25          | 0.0473                             | 0.0471                   | 7.76×10 <sup>-4</sup>    | 0.9999                                    | 0.956    | 0.9641 | 53.1±1.9                | 1                               |
| 0.5           | 0.0508                             | 0.0542                   | 5.49×10 <sup>-4</sup>    | 0.9990                                    | 0.9543   | 0.9538 | 52.60±1.1               | 1                               |
| 1.0           | 0.0312                             | 0.0434                   | 6.89×10 <sup>-4</sup>    | 0.9990                                    | 0.9327   | 0.9551 | 42.4±2.0                | 1.5                             |

**Figure S5.** Kinetic plots of organic acid-catalyzed conversion of xylose into furfural in the DMSO solvent medium. Reaction conditions: 0.25 – 0.5 M xylose with 1.0 M organic acid and 0.1 M  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  catalysts in 50 ml DMSO heated in an oil bath at 120 °C for 5 h with a stirring speed of 200 rpm; (A) 0.25 M; (B) 0.5 M ; (C) 1.0 M. Lines are for model-predicted data, and symbols are for experiment-determined data. X: xylose; FF: furfural; HUM; humin



**Table S5.** Comparison of the activation energy for acid-catalyzed conversion of xylose to furfural in different solvent systems

| Catalyst                                          | Solvent         | Temperature<br>(°C) | Activation Energy<br>(kJ/mol) |                             | Ref.,      |
|---------------------------------------------------|-----------------|---------------------|-------------------------------|-----------------------------|------------|
|                                                   |                 |                     | $k_{1obs}$                    | $k_{2obs}$                  |            |
|                                                   |                 |                     |                               |                             |            |
| <i>p</i> TSA-CrCl <sub>3</sub> ·6H <sub>2</sub> O | DMSO            | 110 - 160           | 81.8                          | 66.5                        | This study |
| Formic acid                                       | Water           | 130 - 200           | 152                           | 161                         | [2]        |
| Acetic acid                                       | Water           | 170 - 210           | 108.6                         | 105                         | [3]        |
| ZSM-5 zeolite                                     | Water           | 140 – 220<br>10 MPa | 134.2                         | -                           | [4]        |
| non-catalyzed                                     | Water<br>(HTLW) | 180 – 220<br>10 MPa | 111.5                         | 143.1                       | [5]        |
| non-catalyzed                                     | Water<br>(HTLW) | 140 – 240<br>3 MPa  | 76.6                          | 153.8/<br>58.8 <sup>a</sup> | [6]        |
| H <sub>2</sub> SO <sub>4</sub>                    | Water           | 155 - 185           | 82.8                          |                             | [7]        |
| HCl                                               | MIBK-water      | 140 -170            | 123.9                         | 72.5                        | [8]        |
| HCl-NaCl                                          | Water           | 160 – 200           | 133.3                         | 125.8                       | [9]        |
| H <sub>2</sub> SO <sub>4</sub>                    | Water           | 145 - 175           | 145                           | -                           | [10]       |
| H <sub>2</sub> SO <sub>4</sub>                    | GVL             | 145 - 175           | 114                           | -                           |            |

<sup>a</sup> The two values represent a combined first- and second-order reaction, respectively.

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