Experimental Section

**Materials:** D-fructose (99%), inulin (from dahlia tubers), 5-hydroxymethylfurfural (5-HMF, 99%), MnCl$_2$$\cdot$4H$_2$O (99%), NiCl$_2$$\cdot$6H$_2$O (99%), LaCl$_3$$\cdot$7H$_2$O (99%), CoCl$_2$$\cdot$6H$_2$O (99%), ZnCl$_2$ (99%), AlCl$_3$$\cdot$6H$_2$O (98%) and InCl$_3$$\cdot$4H$_2$O (99%) were purchased from Aladdin (China). CrCl$_3$$\cdot$6H$_2$O (98%) was purchased from Sigma-Aldrich (China). YCl$_3$$\cdot$6H$_2$O (99%) was purchased from Energy Chemical (China). SnCl$_4$$\cdot$5H$_2$O (99%), P$_2$O$_5$ (98%), Ni(NO$_3$)$_2$$\cdot$6H$_2$O (98%), NiSO$_4$$\cdot$6H$_2$O (98%), Cr(NO$_3$)$_3$$\cdot$9H$_2$O (99%), Cr$_2$(SO$_4$)$_3$$\cdot$6H$_2$O (99%), NaCl (99%), H$_3$PO$_4$ (85 wt%), Na$_3$PO$_4$ (98%), Na$_2$HPO$_4$ (99%), NaH$_2$PO$_4$$\cdot$2H$_2$O (99%), dimethyl sulfoxide (DMSO, 99%) and glycerol (99%) were purchased from Sinopharm (China). Sulfuric acid (H$_2$SO$_4$, 98 wt%) was provided by a local supplier. All of the commercial chemicals were used as received. Purified water (H$_2$O) with a resistivity of 18.2 MΩ-cm was produced by an ultra-pure water system (Taoshi Brand, China).

**Reaction procedure:** Typically, fructose (60 mg), catalyst (10 mol% to fructose) and DMSO (1 mL) were added into a reaction vial with a magnetic stir bar. The vial was sealed and inserted into a heating block. The reaction mixture was stirred at the reaction temperature. After a specified time, the reaction was quenched by immersing the reaction vial in an ice-water bath. The mixture was diluted by water and a certain amount of glycerol (internal standard) was added. A small amount of reaction mixture was taken out, further diluted with water and filtered for analysis.

**Analysis method:** The samples were analyzed by high performance liquid chromatography (HPLC). HPLC was performed on a Shimadzu LC-16 system equipped with a Shimadzu RID-20 refractive index detector and an Agilent Hi-Plex ligand exchange column (H-form, 300×7.7 mm). A 0.005 M aqueous solution of H$_2$SO$_4$ was used as the mobile phase. The flow rate was set to be 0.65 mL/min. The column and detector temperatures were 65 °C and 50 °C, respectively. Glycerol was added as the internal standard for quantitative calculations. Fructose conversion, 5-HMF yield and selectivity were calculated by mole.
**Fig. S1** The conversion of fructose into 5-HMF with different amounts of P₂O₅ (reaction conditions: fructose 60 mg; DMSO 1mL; 80 °C; 30 min).

**Fig. S2** The HPLC chromatograms for the reactions with a) P₂O₅ and NiCl₂•6H₂O, b) P₂O₅ and CrCl₃•6H₂O, c) P₂O₅ and NaCl (reaction conditions: fructose 60 mg; P₂O₅ 10 mol% to fructose; metal chloride 10 mol% to fructose; DMSO 1mL; 80 °C; 30 min).
Table S1 Results on the conversion of fructose over P$_2$O$_5$ and different chromium salts.\[a\]

| Entry | Catalyst                  | Fructose Conv. (%) | 5-HMF Yield (%) | 5-HMF Sel. (%) |
|-------|---------------------------|--------------------|-----------------|---------------|
| 1     | P$_2$O$_5$                | 37                 | 21              | 57            |
| 2     | P$_2$O$_5$+CrCl$_3$·6H$_2$O | 81                 | 67              | 83            |
| 3     | P$_2$O$_5$+Cr(NO$_3$)$_3$·9H$_2$O | 75                 | 49              | 65            |
| 4     | P$_2$O$_5$+Cr$_2$(SO$_4$)$_3$·6H$_2$O | 40                 | 26              | 65            |

\[a\] Reaction conditions: fructose 60 mg; P$_2$O$_5$ 10 mol% to fructose; Cr fraction 10 mol% to fructose; DMSO 1mL; 80 °C; 30 min.

Table S2 Results on the conversion of inulin into 5-HMF in the studied system.\[a\]

| Entry | Temperature (°C) | Time (min) | 5-HMF Yield (%) |
|-------|------------------|------------|-----------------|
| 1     | 80               | 8          | 22              |
| 2     | 80               | 15         | 36              |
| 3     | 80               | 30         | 42              |
| 4     | 80               | 60         | 45              |
| 5     | 90               | 8          | 35              |
| 6     | 90               | 15         | 43              |
| 7     | 90               | 30         | 45              |
| 8     | 100              | 8          | 39              |
| 9     | 100              | 15         | 44              |

\[a\] Reaction conditions: inulin 60 mg; P$_2$O$_5$ 10 mol% to fructose unit in inulin; NiCl$_2$·6H$_2$O 10 mol% to fructose unit in inulin; DMSO 1mL.
Table S3 Results on the conversion of glucose in the studied system.[a]

| Entry | Catalyst                  | Time (min) | Glucose Conv. (%) | 5-HMF Yield (%) |
|-------|---------------------------|------------|-------------------|-----------------|
| 1     | P₂O₅                      | 30         | 10                |                 |
| 2     | NiCl₂·6H₂O                | 30         | 6                 |                 |
| 3     | CrCl₃·6H₂O                | 30         | 11                |                 |
| 4     | P₂O₅+NiCl₂·6H₂O           | 30         | 11                |                 |
| 5     | P₂O₅+CrCl₃·6H₂O           | 30         | 23                | 0.2             |
| 6     | P₂O₅+NiCl₂·6H₂O           | 60         | 23                |                 |
| 7     | P₂O₅+CrCl₃·6H₂O           | 60         | 31                | 0.2             |
| 8     | P₂O₅+AlCl₃·6H₂O           | 60         | 44                | 0.2             |

[a] Reaction conditions: glucose 60 mg; P₂O₅ 10 mol% to glucose; metal chloride 10 mol% to glucose; DMSO 1mL; 100 °C.