

Supporting Information

Direct Synthesis of Hexitols from Microcrystalline Cellulose and Birch over Zirconium (IV)

Phosphate Supported Nickel Catalysts and the Mechanism Study

Table S1. The structure of Bronsted and Lewis acid site of ZrP.

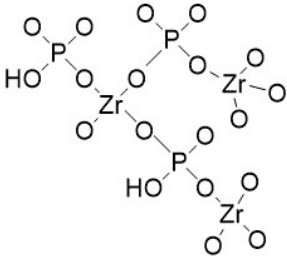
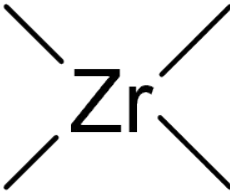
Catalyst	Bronsted site	Lewis site	Ref.
ZrP			1

Table S2. The NH₃ desorption peaks area of screened catalysts.

Catalyst	NH ₃ desorption area
Ni/CeP	4.8042
Ni/TiP	4.9208
Ni/ZrP _{0.5}	7.6843
Ni/ZrP ₁	8.2315
Ni/ZrP _{1.5}	9.5051
Ni/ZrP ₂	15.2321
Ni/ZrP ₃	10.9141

Table S3. Metal contents of Ni/ZrP₂ before and after recycle.

	Content (wt%)
	Ni
Ni/ZrP ₂	19.48
Ni/ZrP ₂ after 3 runs	14.30

Table S4. Metal contents of the solution after reaction.^a

	Content (ug/ml)		
	Ni	Zr	P
Solution after reaction	78.99	None	None

a: The volume of the reaction solution is 10 ml.

Table S5. Element analysis of C, H, N contents in birch wood.

Entry	C (%)	H (%)	N (%)
1	47.65	6.469	0
2	47.66	6.392	0.064
Average	47.66	6.431	0.032

Elemental analysis for C, H, N of birch wood was taken by a Vario ELIII elemental analyzer.

Table S6. The masses of product after conversion of birch wood.

Entry	Substrate	Catalyst	Amount of product (g/biomass-g)			
			Sorbitol	Xylitol	1, 4-Sorbitan	Isosorbide
birch						
1	sawdust	Ni/ZrP ₂	0.2718	0.1582	0.0180	0.0161

Reaction conditions: 150 mg of substrate, 100 mg of Ni/ZrP₂ with Ni loading of 20%, 5 ml of H₂O, 5 ml methanol, 4 MPa H₂, 200 °C, 10 h.

Table S7. The H₂ desorption peaks area of Ni/ZrP₂ with different Ni content.

Catalyst	H ₂ desorption area
5% Ni/ZrP ₂	298.99
10% Ni/ZrP ₂	333.48
15% Ni/ZrP ₂	565.90
20% Ni/ZrP ₂	1295.20
25% Ni/ZrP ₂	901.78
30% Ni/ZrP ₂	887.36

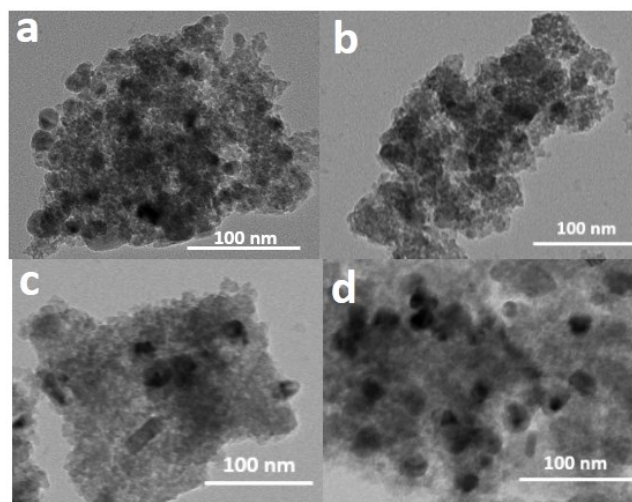


Figure S1. The TEM images of (a) Ni/ZrP_{0.5}, (b) Ni/ZrP₁, (c) Ni/ZrP_{1.5}, and (d) Ni/ZrP₃. The Ni loading of catalysts is 15%.

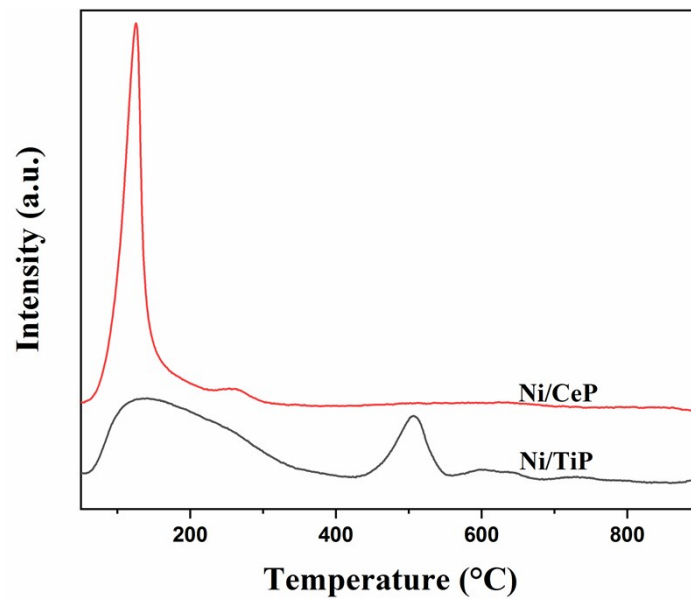


Figure S2. NH_3 -TPD profiles of Ni/CeP and Ni/TiP catalysts. The Ni loading of catalysts is 15%.

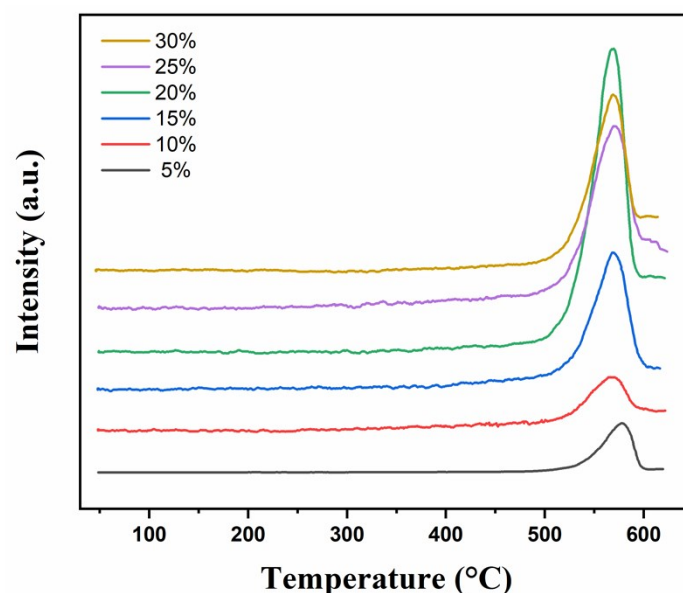


Figure S3. H_2 -TPD profiles for Ni/ZrP₂ with different Ni content.

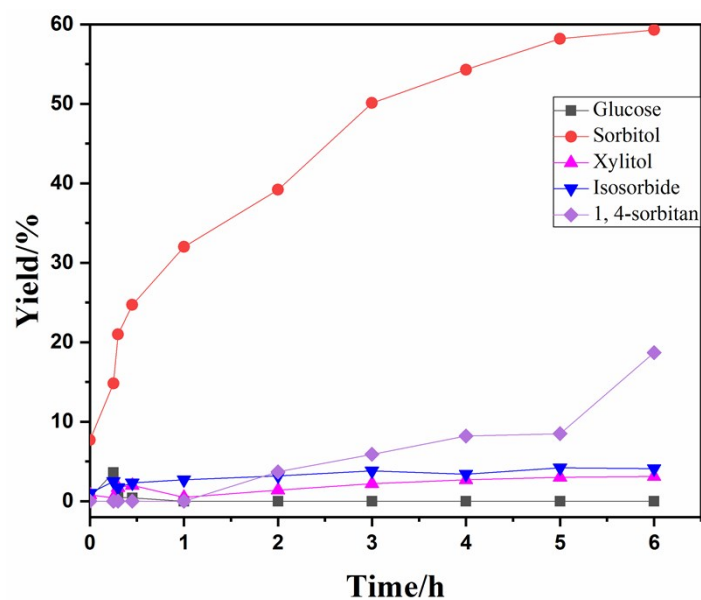


Figure S4. Product distributions of cellulose conversion as function of time. Reaction conditions: 50 mg of microcrystalline cellulose, 50 mg of Ni/ZrP₂ with Ni loading of 20%, 10 ml of H₂O, 4 MPa H₂, 200 °C.

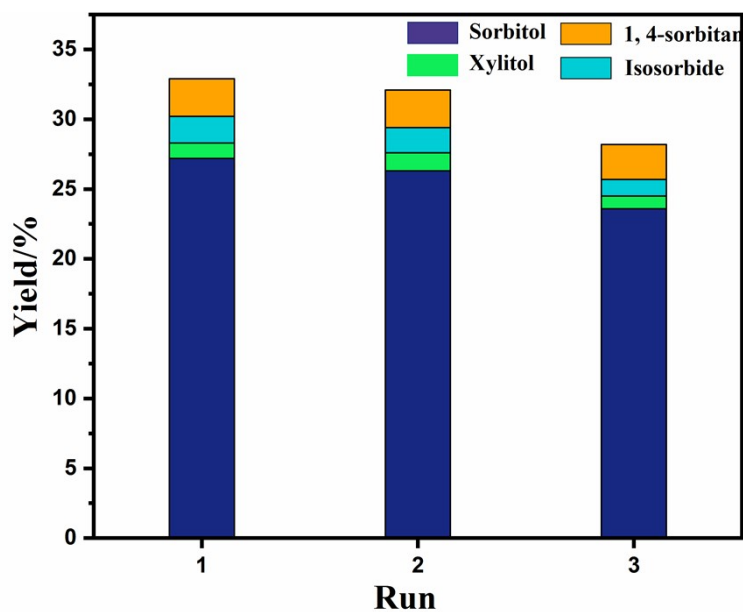


Figure S5. Results of recycle test for MCC conversion. Reaction conditions: 50 mg of microcrystalline cellulose, 50 mg of Ni/ZrP₂ with Ni loading of 20%, 10 ml of H₂O, 200 °C, 4 MPa H₂, 1h.

Reference:

1. Rao, K. N.; Sridhar, A.; Lee, A. F.; Tavener, S. J.; Young, N. A.; Wilson, K., *Green Chem.*, 2006, 8 (9), 790-797.