Supporting Information

Mesoporous ZrO_2 Nanoframes for Biomass Upgrading

Haiqing Wang,[†] Hao Chen,[‡] Bing Ni,[†] Kai Wang,[†] Ting He,[†] Yulong Wu,[§] and Xun Wang*[†]*

† Key Lab of Organic Optoelectronics and Molecular Engineering, Department of Chemistry, Tsinghua University, Beijing 100084, China.

‡ Department of Chemical Engineering, School of Chemical Engineering and Technology, Xi'an jiaotong University, Xi'an 710049, China.

§ Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, China.

Corresponding Author:

* Xun Wang E-mail: wangxun@mail.tsinghua.edu.cn

* Yulong Wu E-mail: wylong@tsinghua.edu.cn

Table S1. Physicochemical properties of catalysts Ni/ZrO_2-F, Ni/ZrO_2-H, and Ni/ZrO_2-C.

Catalysts	Ni loading (wt%)[a]	Ni/Zr[b]	S_{BET} (m^2/g)[c]
Ni/ZrO_2-C	9.9	0.14	39.8
Ni/ZrO_2-H	10.0	0.12	54.8
Ni/ZrO_2-F	9.9	0.11	56.5

a) Determined by ICP. b) XPS result. c) N_2 physisorption result.

Table S2. Catalytic performance of different catalysts over octanoic acid conversion[a]

Catalysts	Conversion /%	Yields /%			
		Heptane	Octane	octanol	Others
Blank	4.9	0.0	0.0	0.8	4.1
ZF-C	19.6	4.3	1.2	6.9	7.2
Ni/ZrO_2-C	54.2	38.7	6.6	3.2	5.6
Ni/ZrO_2-H	86.4	70.3	6.9	2.6	6.3
Ni/ZrO_2-F	100.0	86.0	8.0	3.1	2.8

[a] Reaction conditions: octanoic acid (1 g), decane (100 ml), catalyst (0.1 g), 330 ^{o}C, 3 MPa H_2 and 4 h.

Table S3. Catalytic performance of different catalysts over stearic acid conversion[a]

Catalysts	Conversion /%	Yields /%			
		Heptane	Octane	octanol	Others
Ni/ZrO_2-C	48.1	38.6	5.8	1.5	2.2
Ni/ZrO_2-H	80.3	69.5	7.8	1.3	1.7
Ni/ZrO_2-F	100.0	89.3	7.1	1.2	2.4

[a] Reaction conditions: stearic acid (1 g), dodecane (100 ml), catalyst (0.1 g), 260 ^oC, 3 MPa H_2 and 6 h.

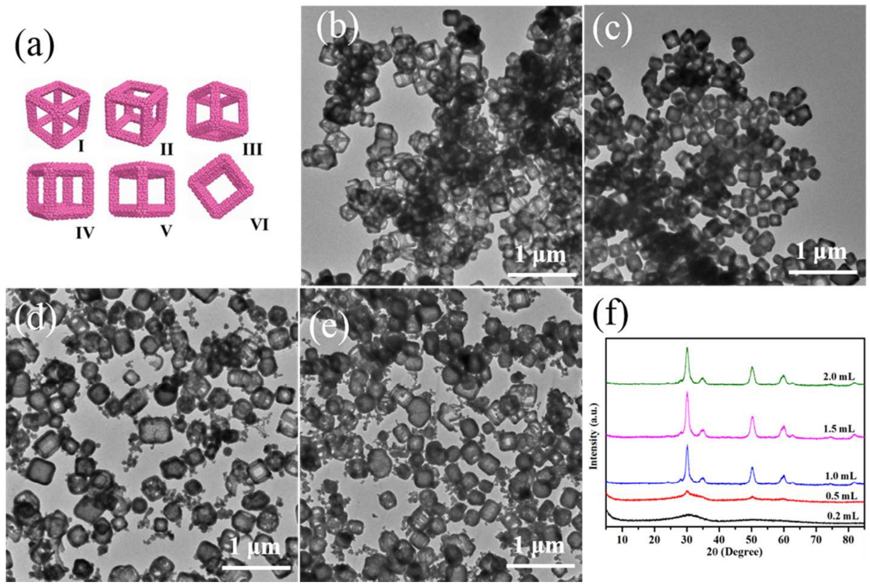

Figure S1. a) Models of ZrO_2 nanoframes (ZFs) with different perspectives, b-e) TEM images of ZFs with varied amounts of ammonia (0.2, 1.0, 1.5, and 2.0 mL), and f) their corresponding XRD patterns.

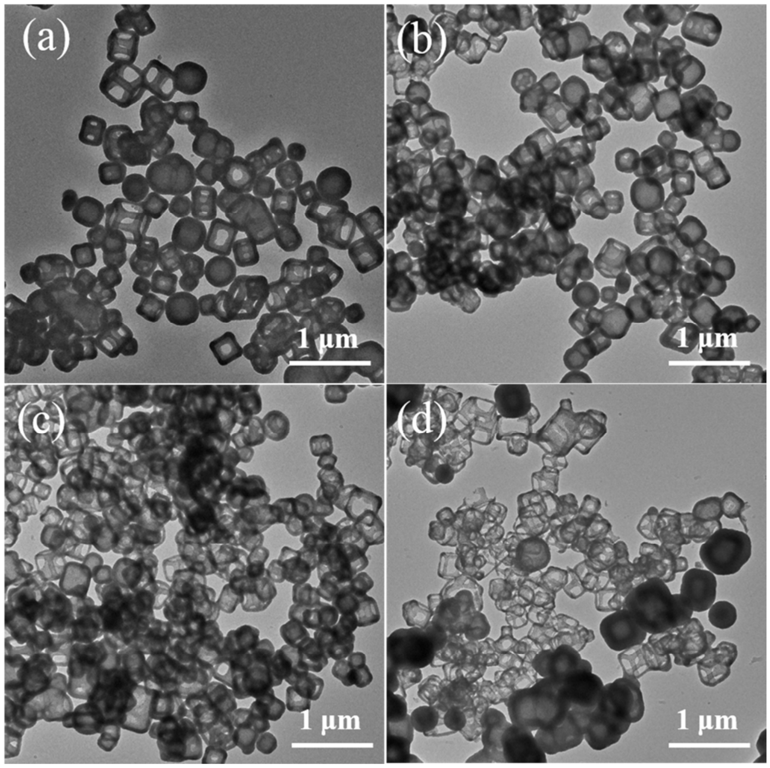

Figure S2. TEM images of ZFs with varied reaction time a) 2 h, b) 8 h, c) 16 h and d) 24 h, respectively.

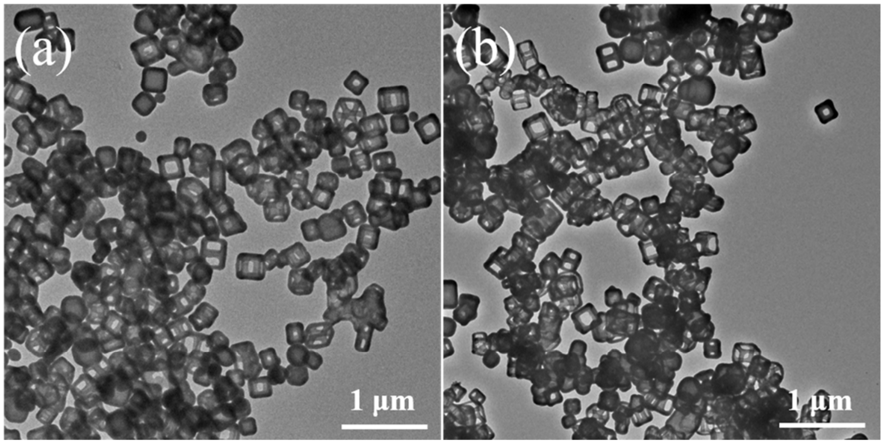

Figure S3. TEM images of ZFs with varied reaction temperatures a) 120 and b) 180 ^{o}C.

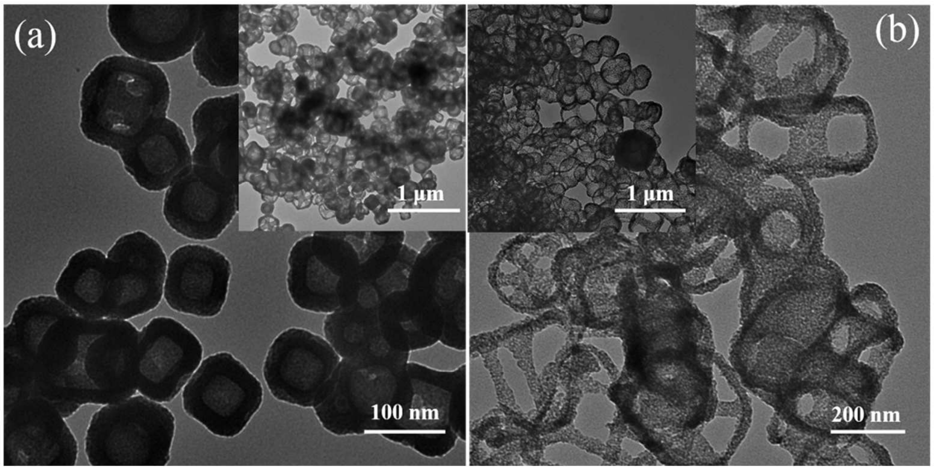

Figure S4. Manipulated size and facet of ZFs with a) cyclohexane and b) hexane.

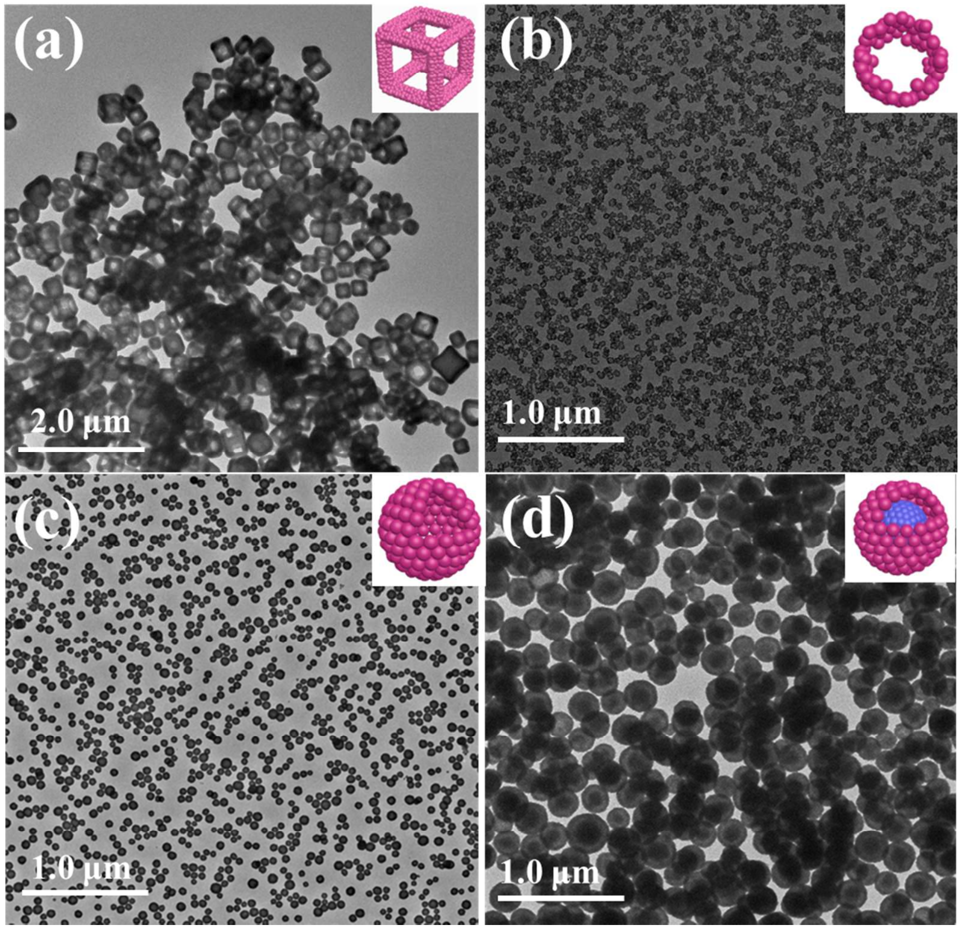

Figure S5. Low-magnification TEM images of a) ZrO_2 nanoframes, b) hollow ring, c) sphere, and d) core-shell in big-scale.

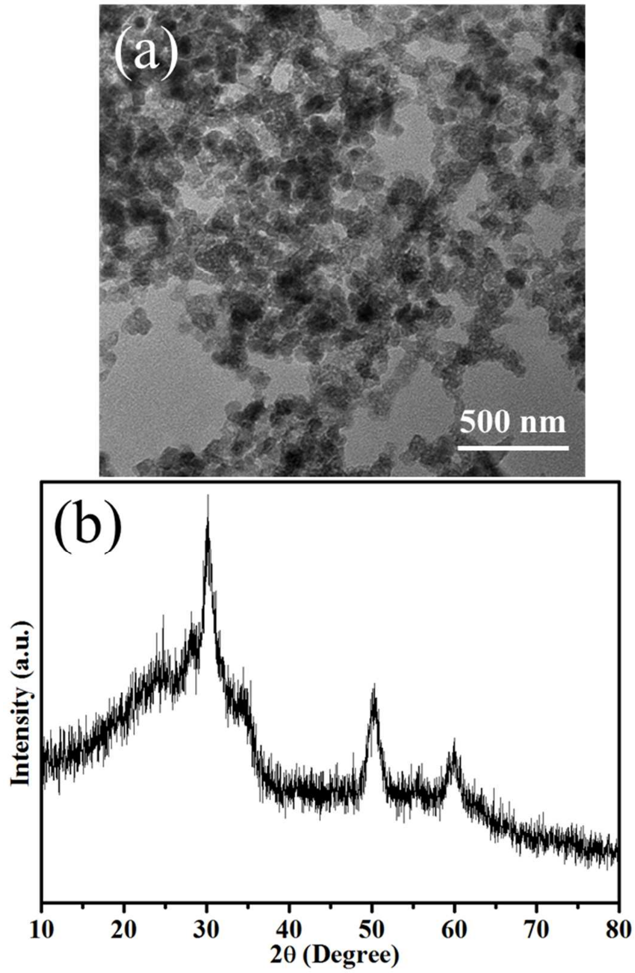

Figure S6. a) TEM image and b) XRD pattern of ZrO_2 nanoparticles synthesized with $ZrCl_4$ as zirconium source.

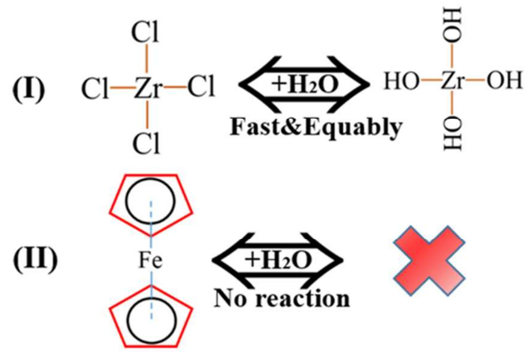

Figure S7. General hydrolysis processes of $ZrCl_4$ (I) and ferrocene (II).

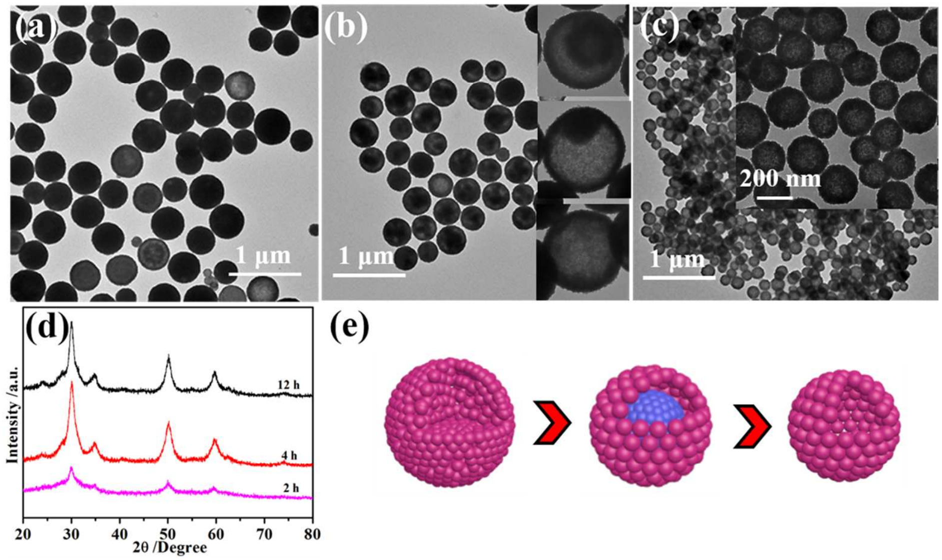

Figure S8. a-c) TEM images of time-dependent intermediates for ZrO_2 hollow sphere (2h, 4h and 12h), d) their corresponding XRD patterns, and e) models of structural transformation.

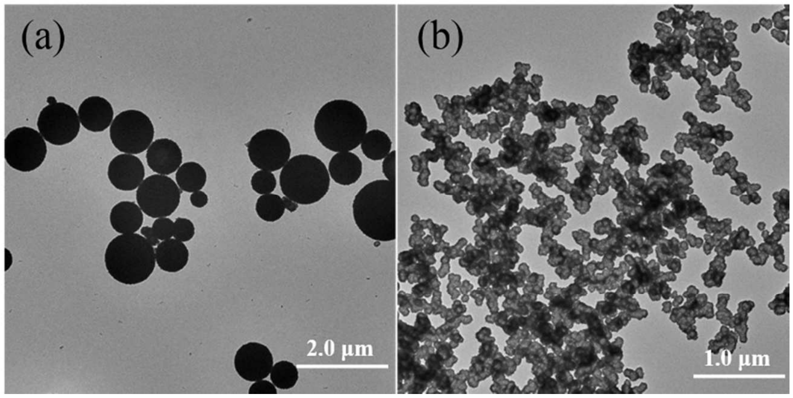

Figure S9. TEM images of ZrO_2 nanostructures synthesized with the same amounts of a) water and b) NaOH replacing ammonia.

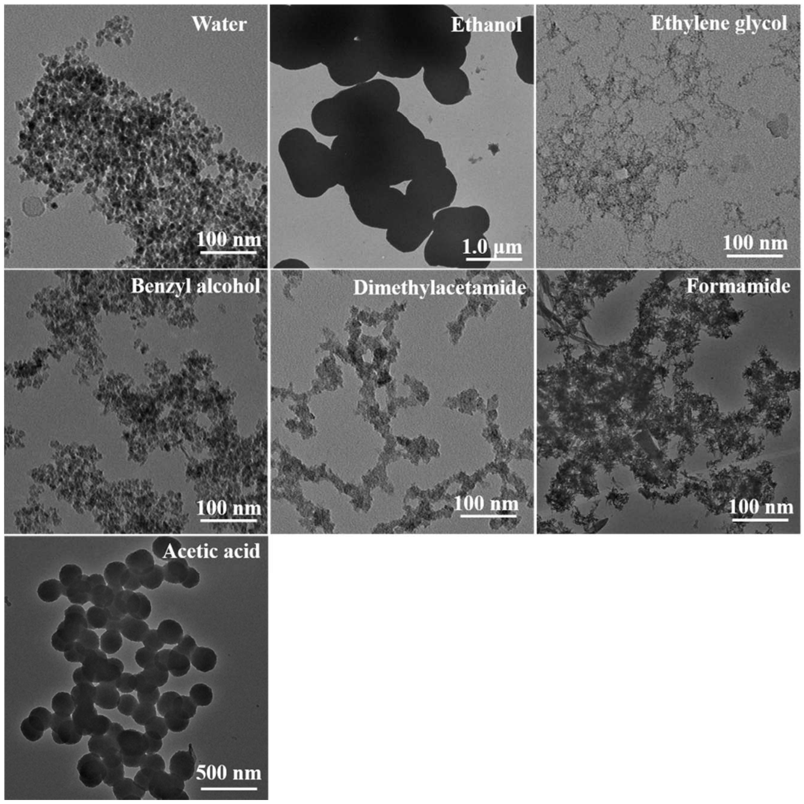

Figure S10. TEM images of ZrO_2 nanostructures synthesized with other kinds of solvents.

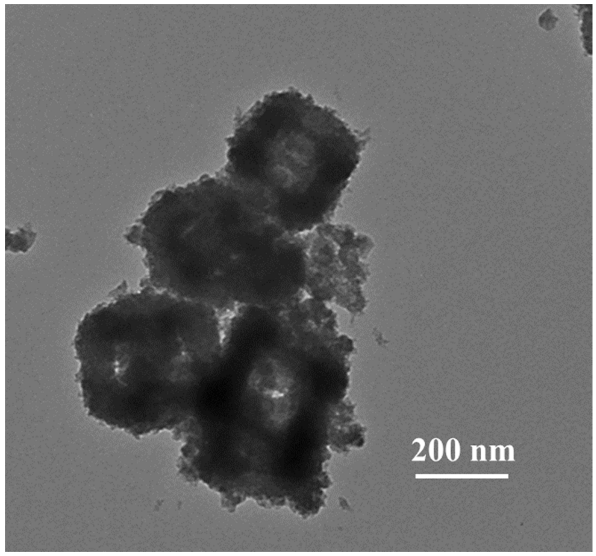

Figure S11. TEM image of ZF intermediate after water watching.

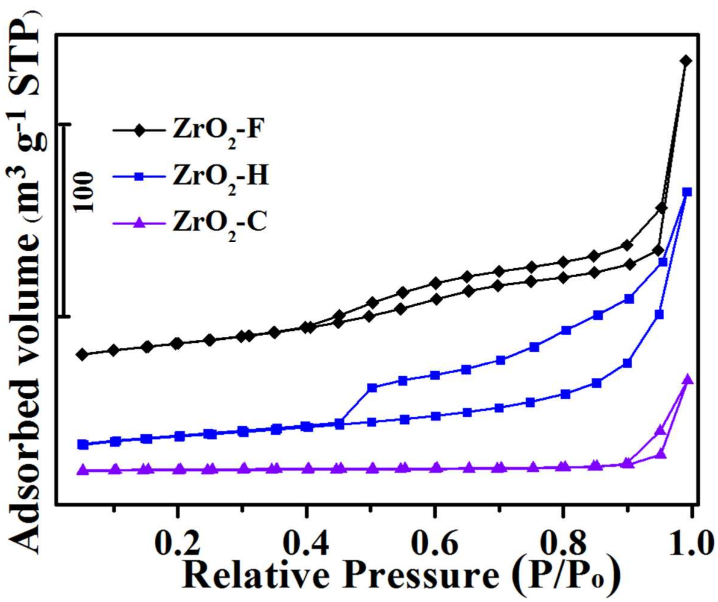

Figure S12. Nitrogen physisorption curves for ZrO_2-F, ZrO_2-H, and ZrO_2-C calcined at 500 ^oC for 2 h before Ni impregnation.

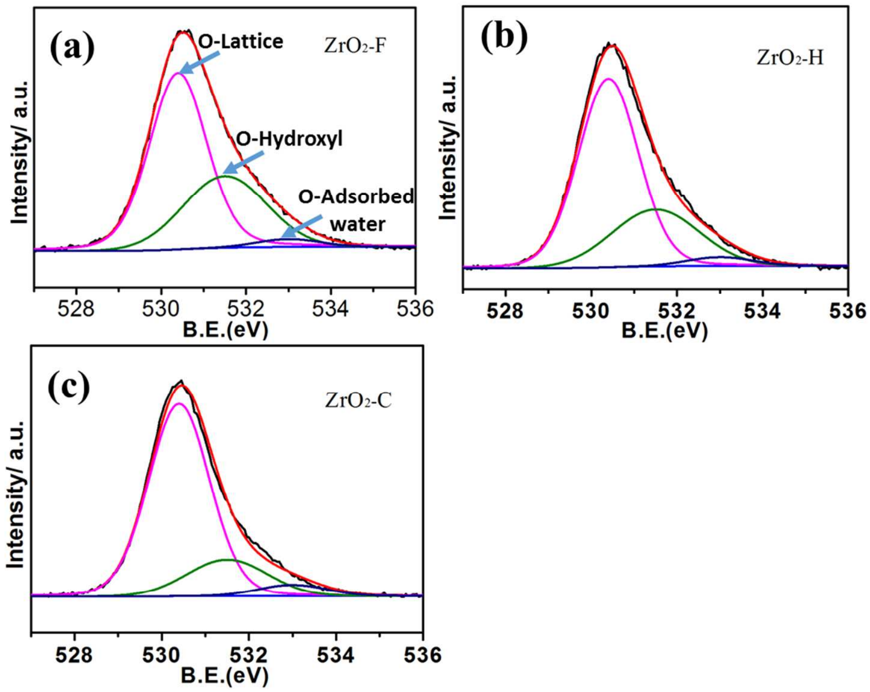

Figure S13. XPS results of (a) ZrO_2-F, (b) ZrO_2-H and (c) ZrO_2-C (Oxygen-lattice, 530.4 eV; Oxygen-hydroxyl, 531.5 eV; Oxygen-adsorbed water, 533 eV)

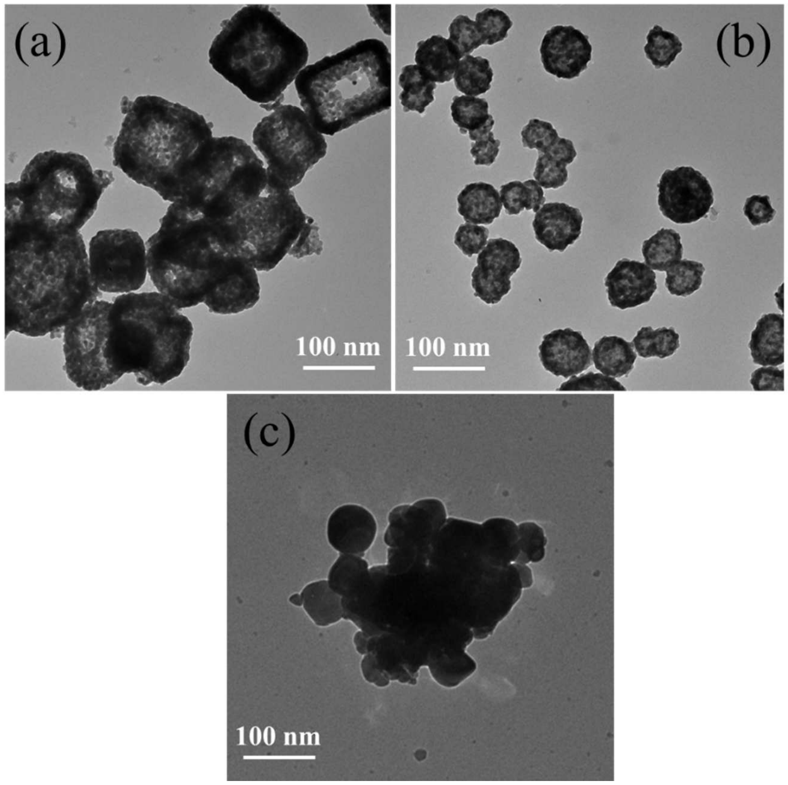

Figure S14. TEM images of a) Ni/ZrO_2-F, b) Ni/ZrO_2-H and c) Ni/ZrO_2-C catalysts.

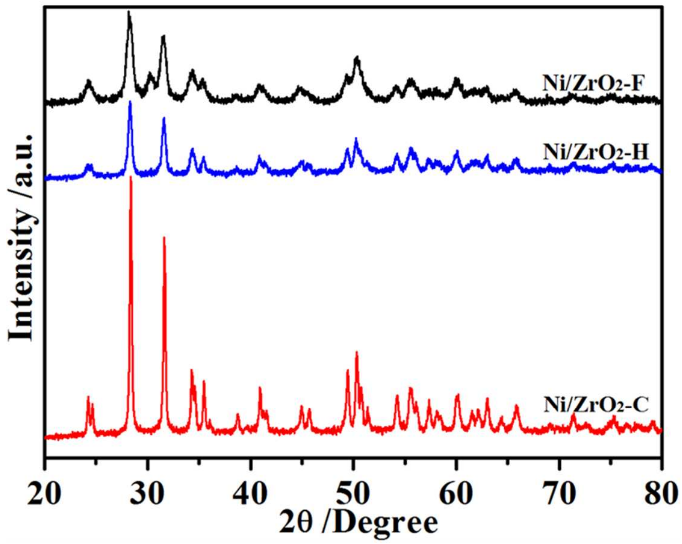

Figure S15. XRD patterns of Ni/ZrO_2-F, Ni/ZrO_2-H and Ni/ZrO_2-C catalysts.

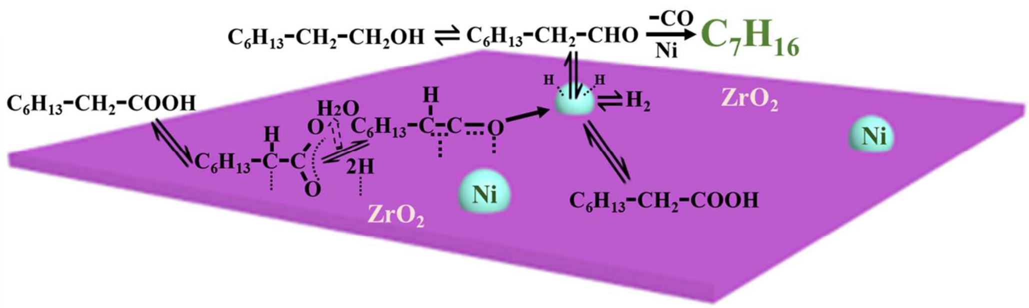

Figure S16. The possible reaction process of upgrading bioacids into alkanes. Reproduced with permission from ref 1. Copyright 2012 American Chemical Society.

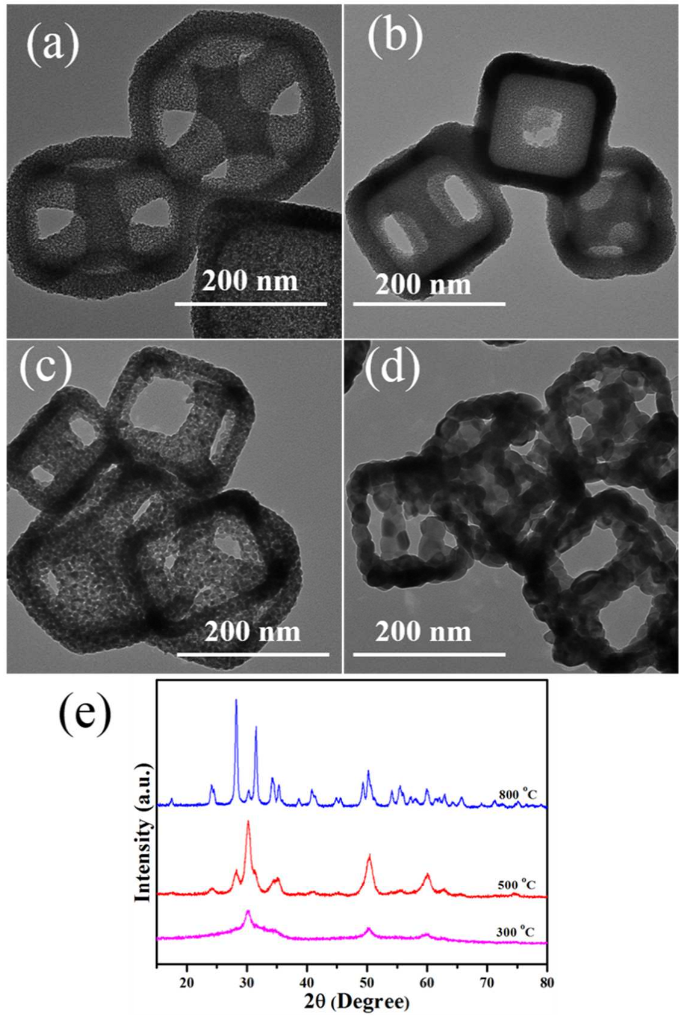

Figure S17. TEM images of ZFs calcined with different temperatures for 2 h, a) 300 °C, b) 400 °C, c) 500 °C, and d) 800 °C, and e) their corresponding XRD patterns.

Reference

1. Peng, B.; Yuan, X.; Zhao, C.; Lercher, J. A., Stabilizing Catalytic Pathways Via Redundancy: Selective Reduction of Microalgae Oil to Alkanes. *J. Am. Chem. Soc.* **2012**, *134*, 9400-9405.