Supplementary Information

Bridging and terminal hydroxyl groups of $Zr(OH)_4$ as active sites for the ultraselective transformation of biomass-based alcohols

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Experimental

1. Materials

All commercially available reagents and solvents were used without any further purification.

2. Preparation of Catalysts

$Zr(OH)_4$ was prepared by placing commercially available Zirconium hydroxide powder in a drying oven at 150 °C for 12 h. $Zr(OH)_4$-H_2SO_4 was prepared by stirring $Zr(OH)_4$ and 0.5M H_2SO_4 solution for 2 h at room temperature, then centrifuging and washing with deionized water, the solid was drying at 150 °C for 12 h. $Zr(OH)_4$-NH_3 was prepared by treating $Zr(OH)_4$ with pure ammonia gas at 150 °C for 5 h in vertical tubular furnace. $Zr(OH)_4$-C_3H_9ClSi was prepared by treating $Zr(OH)_4$ with trimethylchlorosilane in toluene solvent under N_2 atmosphere at 115 °C for 24 h, then it was placed in a vacuum drying oven at 60 °C for 12 h.

3. Characterizations of Catalysts

The crystallographic structure of the solid samples was investigated at room temperature using powder X-ray diffraction (XRD, Rigaku D/max-2400 diffractometer, Cu-Kα radiation,) at a scanning rate of $30^{\circ}\cdot min^{-1}$. The morphology, elemental analysis mapping of the solid samples was examined using transmission electron microscopy (TEM, Tecnai G2 F30, 300 kV), and high-resolution transmission electron microscopy (HRTEM/EDX, Tecnai G2 F30, 300 kV). Raman spectra were recorded on an in Via Renishaw confocal microscope with 633 nm laser excitation. Chemical bonding information of the samples was acquired with Fourier transform infrared spectroscopy (FT-IR, Nicolet NEXUS 670) using the potassium bromide (KBr) pellet technique. To make the KBr pellets, about 1 mg of sample was diluted with 100 mg of KBr powders. Each FTIR spectrum was collected after 32 scans with a resolution of 4 cm^{-1} from 400 to 4000 cm^{-1}. X-ray photoelectron spectroscopy (XPS) was performed on the PHI-5702 instruments with an Mg anode (Mg Kα hυ = 1253.6 eV) at a base pressure of 5×10^{-8} mbar. The revision of the binding energies (BE) was implemented with the C1s peak of extraneous C at 284.6 eV. Solid-state ^{1}H MAS NMR spectra were obtained on a Bruker AVANCE II 400 WB spectrometer. The spinning speed was 10 kHz. All chemical shifts are referenced to TMS externally. ^{1}H MAS NMR signal is collected using a pulse width of 3 μs. Thirty-two scans were sufficed to provide a satisfactory signal-to-noise ratio in the NMR spectrum. Thermogravimetric analysis (TGA) was performed on TGA TA-Q50 (METTLER TOLEDO). Inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Optima-4300DV) was used to measure Zr leaching in the filtrate after catalyst recovery.

4. Test of Catalytic Activity

In a typical experiment, catalyst, corresponding alcohol substrate and solvent were added into a stainless-steel reactor, followed by pressurizing it to required molecular oxygen or nitrogen pressure. Then the mixture was stirred and heated to setting temperature for a desired period of time. After the completion of the reaction, the autoclave was cooled to room temperature. The remaining oxygen was discharged and the sample was removed from the autoclave. Subsequently, the crude mixture was diluted with ethyl acetate and filtered, the product mixture was identified by GC and GC-MS.

In the recycle experiment, the catalyst was collected by centrifugation, and exhaustively washed with ethyl acetate and ethanol. Then it was placed in a drying oven at 60 °C for 12 h. The spent catalyst was used for the next run under the same conditions. Other cycles were repeated with the same procedure.

5. Computational Details

Gaussian 09 package[1] was used in geometry optimization and electronic structure calculations of 1-phenylethanol, $Zr(OH)_4$ cluster and the adsorption complex formed between $Zr(OH)_4$ cluster and 1-phenylethano. A dispersion energy correction was added to the hybrid B3LYP exchange correlation functional via the DFT-D3 model.[2, 3] For H, C and O atoms, the 6-31g (d, p) basis set[4] was used, while for Zr atom, the LANL2DZ basis set[5] was used. Berny algorithm[6] was used to search transition-state (TS). Vibrational frequency calculation was performed at the same level of theory to confirm that each reaction intermediates has no imaginary frequency, while each transition-state has only one imaginary frequency.

Supporting results

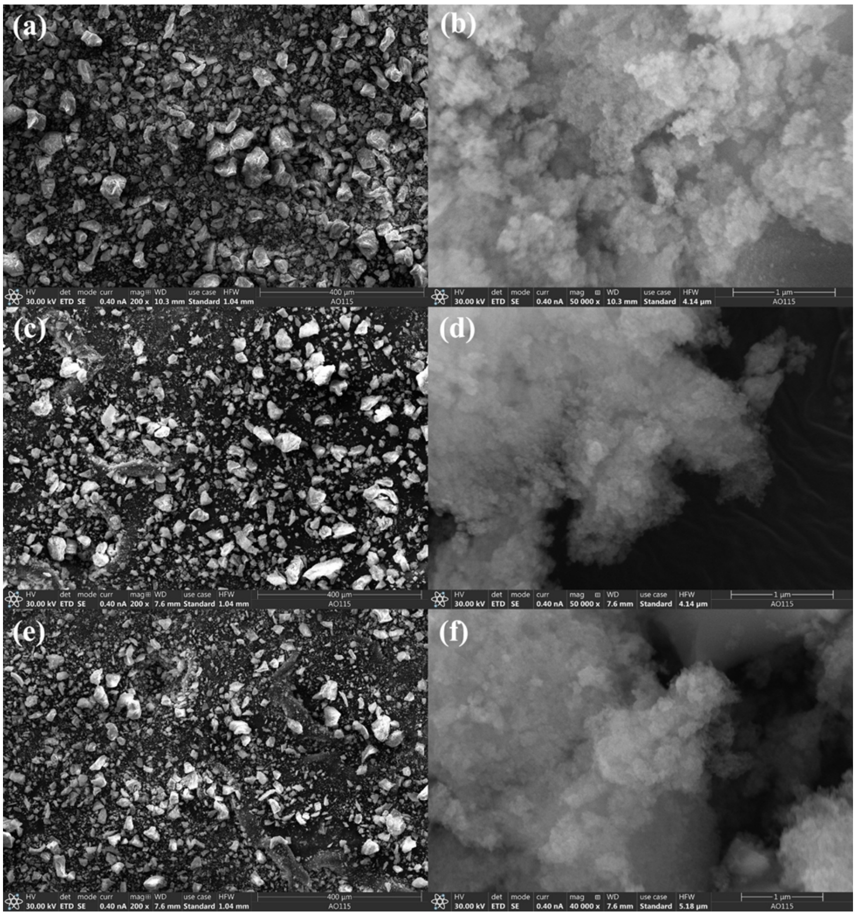

Figure S1. Scanning electron microscope (SEM) figures of fresh $Zr(OH)_4$ (a, b) and six times reused $Zr(OH)_4$ after oxidative dehydrogenation (c, d) and dehydration reaction (e, f).

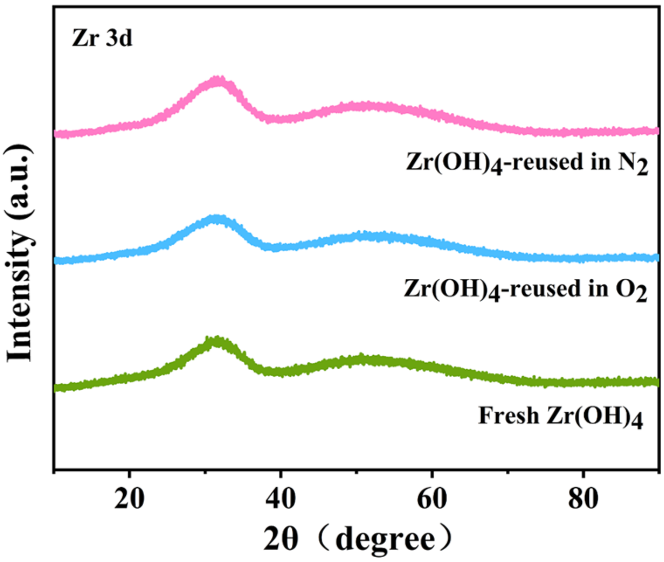

Figure S2. XRD patterns of fresh $Zr(OH)_4$ and six times reused $Zr(OH)_4$ after oxidative dehydrogenation and dehydration reaction.

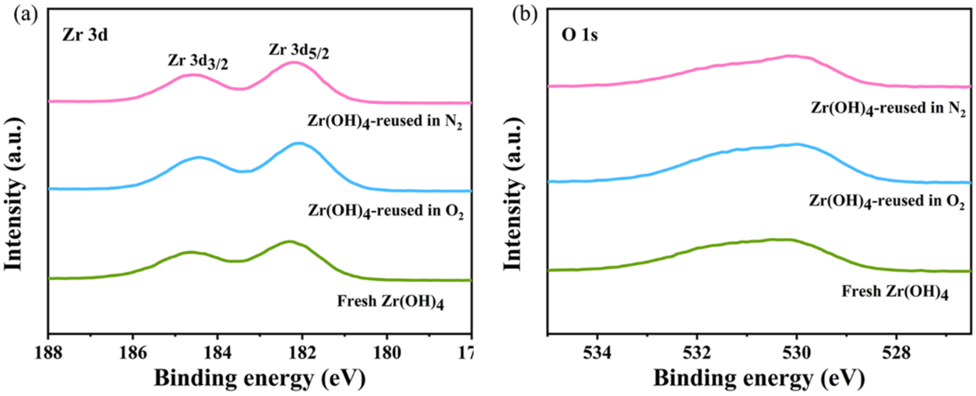

Figure S3. Zr 3d (a) and (b) O 1s XPS spectra of fresh $Zr(OH)_4$ and six times reused $Zr(OH)_4$ after oxidative dehydrogenation and dehydration reaction.

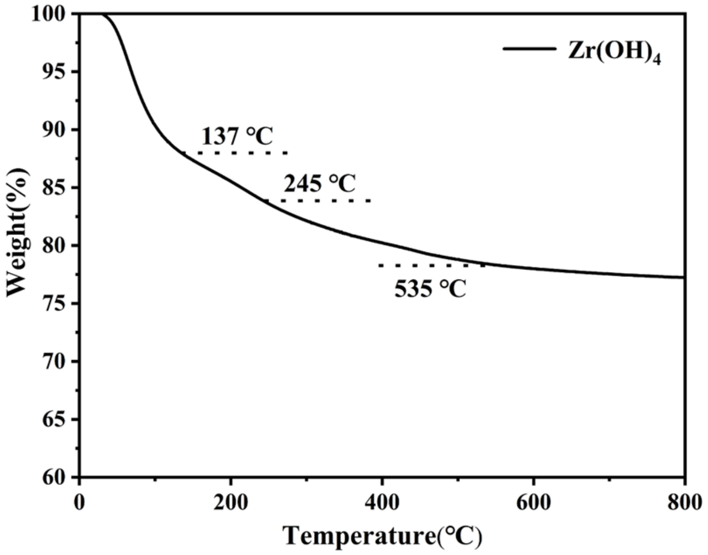

Figure S4. TGA curve of the $Zr(OH)_4$ catalyst.

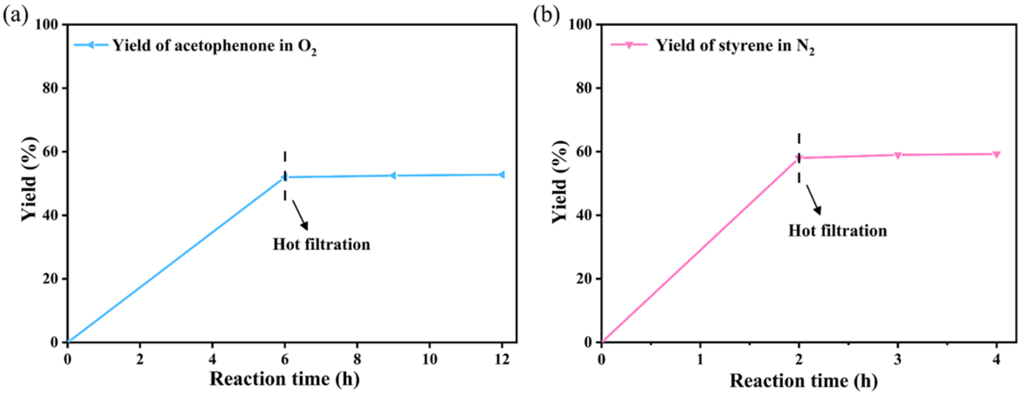

Figure S5. Hot filtration experiments of $Zr(OH)_4$ by continuing the reaction after filtration of the catalyst. Reaction conditions: (a) 1-phenylethanol (1 mmol), $Zr(OH)_4$ (50 mg), solvent (toluene 5 mL), 800 rpm, 150 ^{o}C, 1 MPa O_2. (b) 1-phenylethanol (1 mmol), $Zr(OH)_4$ (50 mg), solvent (dichloromethane 5 mL), 800 rpm, 150 ^{o}C, 1 MPa N_2.

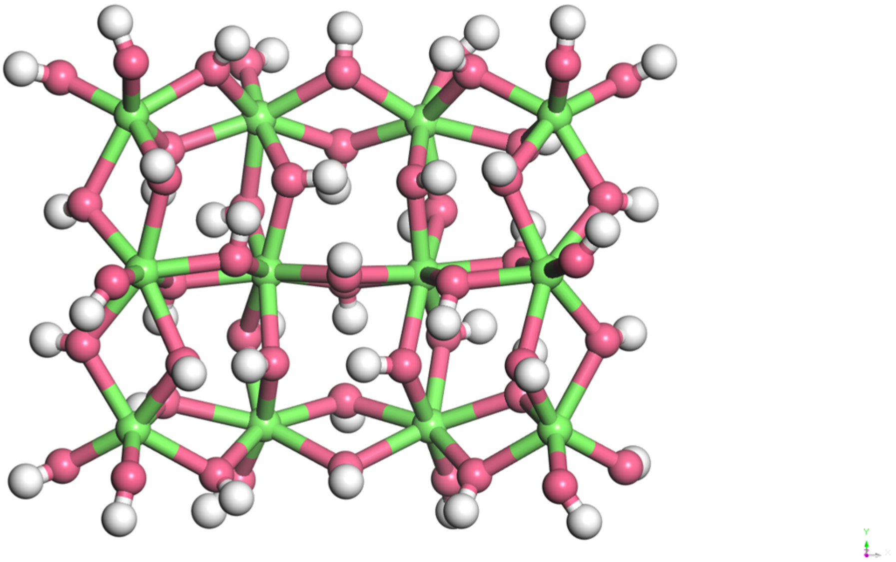

Figure S6. The optimized structural model of $Zr(OH)_4$.

The detail optimized Cartesian coordinates (in Å) of stationary states are listed as following:

Structural model :

Zr	4.73330000	3.52100000	0.69680000
Zr	1.75900000	3.37920000	-1.44260000
Zr	-1.91570000	3.46470000	-1.39520000
Zr	-4.77420000	3.52770000	0.86520000
Zr	4.54160000	0.00410000	1.70090000
Zr	1.77030000	-0.02330000	-0.48410000
Zr	-1.74220000	0.02270000	-0.53120000
Zr	-4.53380000	0.02660000	1.65830000
Zr	4.73520000	-3.51920000	0.91950000
Zr	1.92350000	-3.43450000	-1.41070000
Zr	-1.81120000	-3.40320000	-1.42740000
Zr	-4.73880000	-3.50800000	0.74400000
O	4.02120000	2.83220000	-1.21390000
O	-0.05860000	2.83450000	-2.45000000
O	-3.96350000	2.76830000	-0.98370000
O	3.92090000	0.18660000	-0.43160000
O	0.02330000	-0.18830000	-1.73220000
O	-3.89590000	-0.21130000	-0.45790000
O	3.99200000	-2.75280000	-0.94850000
O	0.02130000	-2.87640000	-2.54470000
O	-4.06220000	-2.88750000	-1.19720000

O	2.84010000	4.50520000	0.19290000
O	-0.02060000	4.49440000	-0.63890000
O	-2.95020000	4.56850000	0.21820000
O	2.45000000	-0.22760000	1.64930000
O	0.00700000	-0.05820000	0.74070000
O	-2.44710000	0.29640000	1.58860000
O	2.93280000	-4.55650000	0.21340000
O	0.03120000	-4.40060000	-0.62350000
O	-2.86630000	-4.53760000	0.19410000
O	5.87400000	1.64550000	0.97750000
O	2.15110000	1.37870000	-2.21470000
O	-2.18200000	1.40570000	-2.22200000
O	-5.82500000	1.52530000	0.75470000
O	5.81720000	-1.52370000	0.82970000
O	2.23990000	-1.41910000	-2.21790000
O	-2.23250000	-1.42890000	-2.24850000
O	-5.87250000	-1.62960000	0.97660000
O	3.62010000	2.09480000	1.92960000
O	1.57610000	2.03090000	0.23200000
O	-1.23320000	2.07200000	0.05940000
O	-4.03920000	2.12340000	2.32400000
O	4.01140000	-2.08960000	2.39180000
O	1.34440000	-2.08680000	0.10540000
O	-1.62390000	-2.03810000	0.19310000
O	-3.61370000	-2.05950000	1.93340000
H	4.52800000	3.02380000	-2.01180000
H	-0.23830000	1.92030000	-2.71780000
H	-4.16530000	1.84100000	-1.17780000
H	4.13710000	0.99810000	-0.94240000
H	0.13560000	-0.99980000	-2.26930000
H	-4.12340000	-1.01800000	-0.96670000
H	4.17660000	-1.80780000	-1.07300000
H	0.08380000	-3.20540000	-3.45040000
H	-4.56460000	-3.08430000	-1.99600000
H	2.31200000	4.90370000	0.89510000
H	0.02040000	5.45560000	-0.71220000
H	-2.50730000	5.13910000	0.85610000
H	2.23550000	-1.13060000	1.93170000
H	0.01500000	0.27880000	1.64070000
H	-2.25930000	1.21600000	1.83470000
H	2.63160000	-5.34990000	0.66820000
H	0.04680000	-4.68840000	0.29700000
H	-2.41850000	-5.06040000	0.86860000
H	6.66480000	1.52180000	0.44010000

H	1.59270000	1.05100000	-2.92940000
H	-2.92530000	1.17860000	-2.79170000
H	-6.34320000	1.36550000	-0.04330000
H	6.40760000	-1.36640000	0.08380000
H	3.04320000	-1.21270000	-2.70840000
H	-1.71280000	-1.18710000	-3.02340000
H	-6.66610000	-1.51100000	0.44250000
H	3.49270000	2.31710000	2.86000000
H	2.12580000	2.12720000	1.04620000
H	-0.31540000	2.14180000	0.38500000
H	-4.18810000	2.38940000	3.24090000
H	4.21510000	-2.29990000	3.31260000
H	0.44520000	-2.07530000	0.48030000
H	-2.13410000	-2.09050000	1.03520000
H	-3.48190000	-2.26800000	2.86670000
O	6.28160000	4.30730000	-0.29260000
O	2.39000000	4.72400000	-2.75720000
O	-2.21550000	4.68310000	-2.92510000
O	-6.38430000	4.37050000	0.08930000
O	5.21680000	0.26860000	3.54950000
O	-5.20870000	-0.22050000	3.51160000
O	6.32210000	-4.37020000	0.06180000
O	2.35440000	-4.62860000	-2.90600000
O	-2.38480000	-4.64900000	-2.85440000
O	-6.32400000	-4.34090000	-0.12820000
H	7.07900000	4.71970000	0.05370000
H	3.09340000	5.37640000	-2.67200000
H	-1.63380000	4.87450000	-3.66870000
H	-7.25560000	4.56550000	0.44720000
H	5.81030000	0.95400000	3.87470000
H	-5.77370000	-0.93010000	3.83610000
H	6.49150000	-4.28170000	-0.88330000
H	2.45310000	-5.35630000	-3.52110000
H	-3.03070000	-5.34620000	-2.99610000
H	-7.14990000	-4.68290000	0.22670000
O	4.92520000	4.66680000	2.30970000
O	-4.78180000	4.70880000	2.50090000
O	4.85250000	-4.79760000	2.45470000
O	-4.83900000	-4.61160000	2.40270000
H	5.02580000	5.60120000	2.50980000
H	-5.13840000	5.60370000	2.50690000
H	5.39920000	-5.59130000	2.42740000
H	-5.05160000	-5.53110000	2.58540000

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