Ordered, Extra-large Mesoporous Ceramic Acid with Strong Brönsted Acid Sites and Excellent Thermal/hydrothermal Stability

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Supporting Information:

Material Synthesis:

EP-$WZrO_x$-T (T indicated the calcination temperature in °C):

The procedure is similar to the recently developed method for the preparation of extra-large mesoporous metal oxides (S. Xu, Y. Hong, C. Chen, S. Li, L. Xiao and J. Fan, J. Mater. Chem. A, 2013, 1, 6191-6198). In a typical synthesis, 1 mmol Zirconium(IV) 80 wt% butoxide solution and 0.11 mmol WCl_6 , 2.4 ml Acetic acid (HOAc), 2 ml HCl solution (12 M) and 5.4 g of mesoporous silica EP-FDU-12 (9 mmol) were dissolved in 30 ml ethanol. The mixture was stirred vigorously for 1~2 h and then transferred into a Petri dish. The ethanol was evaporated at 40 °C with a relative humidity of ~ 40 %. After 12 h, it was transferred into a 65 °C oven and aged for an additional 24 h. The obtained samples were calcined at different temperatures (800~1000 °C, ramp rate 4 °C min^{-1}).

$WZrO_x$-T (T indicated the calcination temperature in °C):

9 mmol Zirconium (IV) 80 wt% butoxide solution and 1 mmol WCl_6, 2.4 ml Acetic acid (HOAc), 2 ml HCl solution (12 M) and 1.6 g of F127 ($EO_{106}PO_{70}EO_{106}$, MW = 12600 g/mol) were dissolved in 30 ml ethanol. The mixture was stirred vigorously for 1~2 h and then transferred into a Petri dish. The ethanol was evaporated at 40 °C with a relative humidity of ~ 40 %. After 12 h, it was transferred into a 65 °C oven and aged for an additional 24 h. The obtained samples were calcined at different temperatures (800~1000 °C, ramp rate 4 °C min^{-1}).

Al-SBA-15-1000

1 mmol (0.25 g) of aluminum tri-*sec*-butoxide, 2.3 ml of acetic acid (HOAc), 1 ml of HCl solution (12 M) and 9 mmol (0.54 g) SBA-15 were dissolved in 30 ml of ethanol. The mixture was stirred vigorously for 1–2 h and then transferred into a Petri dish. The ethanol was evaporated at 40 °C with a relative humidity of ~40 %. After 12 h, it was transferred into a 65 °C oven and aged for an additional 24 h. The obtained samples were calcined at 1000 °C (ramp rate 4 °C min^{-1}).

Characterization Methods:

XRD patterns were recorded on a Bruker D8 diffractometer operated at 40 mA and 40 kV with Cu K_a radiation with a step size of 0.02° and a scan rate of 2.5 s/step. The Raman spectroscopy was used to obtain the molecular structures of catalysts with a visible (514.5 nm) laser excitation on JobinYvon–Lab. HR800 Raman spectrometer was equipped with a confocal microscope (LMPlanFI 50*/0.50, JAPAN) and a cooled CCD detector (77 K) with a spectral resolution of 1 cm^{-1}. The visible excitation was generated by a Ar excitation light source. The laser power was adjusted to 10 mW. Nitrogen adsorption-desorption analysis was carried out at 77 K on a Micromeritics ASAP 2020 adsorption analyzer. Before the adsorption analysis, the samples were out gassed under a vacuum at 200 °C in the port of the adsorption analyzer. The TEM images were taken using a JEOL 1230 electron microscope operating at 80~120 kV. HAADF-STEM images and elemental mapping were recorded on the TECNAI G2 F20 operated at 200 kV. The sample was embedded in epoxy resin, and then microtomed into sub-100 nm ultra thin film at room temperature. These thin film samples floating on water or other solvents were collected by a copper mesh with a polymer microgrid for HAADF-STEM image and elemental mapping.

The acid site concentration and distribution of the catalysts were determined by temperature programmed desorption of ammonia (NH_3-TPD) on a Micromeritics ActoChem II 2920 equipment. The granular sample (100 mg) was pretreated at 300 ^{o}C (ramp rate 10 ^{o}C min^{-1}) in a quartz reactor for 2 h in flowing He (30 ml min^{-1}), cooled down to 80 ^{o}C, treated with a stream of mixture gas (10% NH_3 in He), and flushed with He until physisorbed NH_3 was completely removed. The NH_3-TPD temperature program was carried out from 100 to 800 ^{o}C (ramp rate 15 ^{o}C min^{-1}) and finally the ammonia desorption was continuously measured by gas chromatography using a thermal conductivity detector.

The quantity and strength of the acid sites (Brönsted acid sites and Lewis acid sites) were determined by means of Fourier transform infrared (FT-IR) spectrum of pyridine adsorption (Py-IR). The catalysts (~11 mg) were pressed into thin self-supported wafers followed by pre-heated at 400 ^{o}C for 1.5 h under 10 $^{-5}$ torr vacuum. Then, after cooling to room temperature, the samples adsorbed pyridine vapor for 30 min at 25 ^{o}C. Finally, the samples were exposed to vacuum (10^{-5} torr) at 150 ^{o}C for 1 h, and then the FT-IR spectra of pyridine adsorption were collected.

Hydrothermal stability evaluation:

The calcined samples (EP-WZrO$_x$-800 and WZrO$_x$-800) were placed in the center of a quartz tube of the furnace. The samples were heated to 300 ^{o}C with a ramp rate of 4 ^{o}C min^{-1}. Afterwards, a 20 % water steam flow produced by heating a flask containing deionized water was passed through the tube furnace for 24 h. The steamed samples were denoted as EP-WZrO$_x$-800-W and WZrO$_x$-800-W.

F-C reaction of anisole and benzyl alcohol:

The reaction was performed using 0.1 g of catalyst, 50 mmol of anisole, and 5 mmol of benzyl alcohol in an oil bath at 120 ^{o}C. 50 μL of solution was taken out from the reaction solution each one hour. The solution was centrifuged and mixed with 500 μL of ethanol, to which 50 μL n-decane was added as an internal standard.

The concentration of each substrate was analyzed by a gas chromatograph (GC-9790, Fuli) equipped with a capillary column.

Table S1:

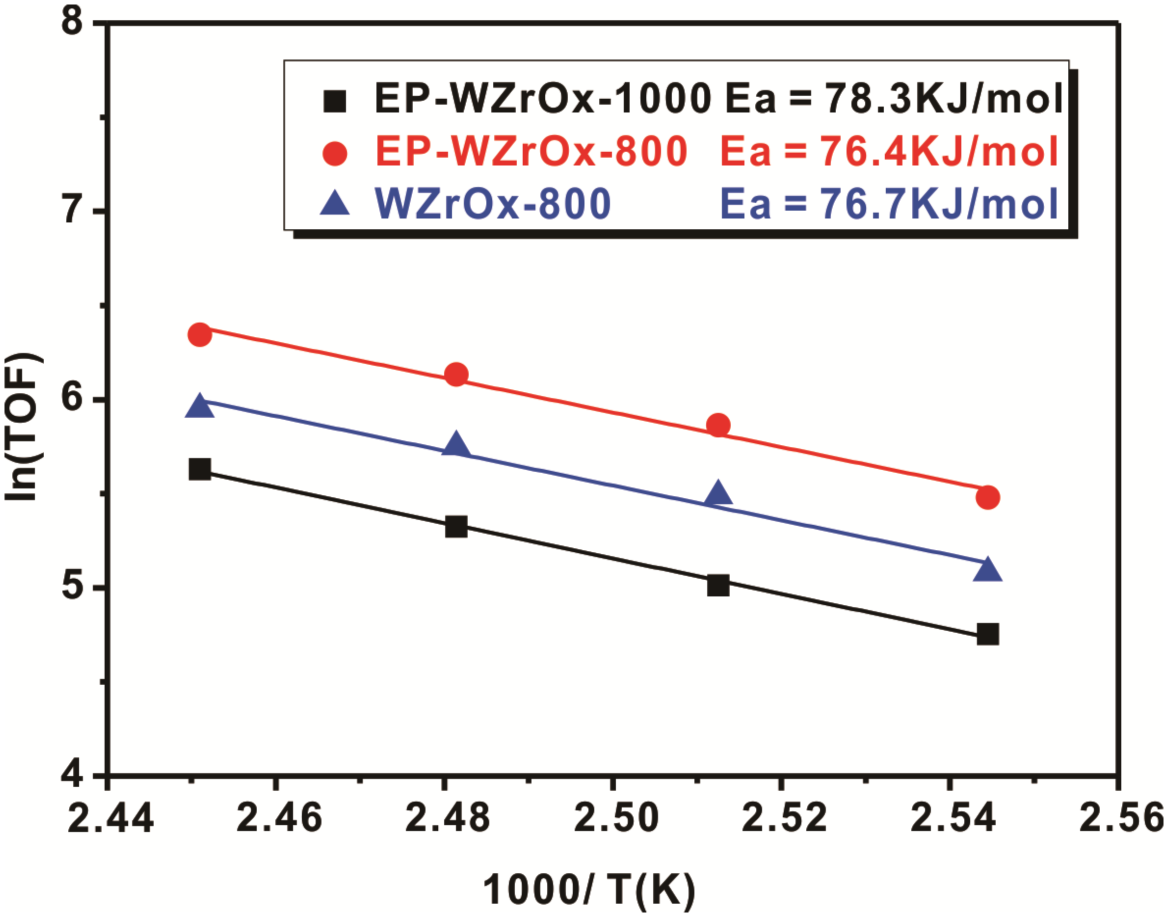
Sample	S_{BET} (m^2/g)	Pore size (nm)	W density ($atom/nm^2$)
EP-WZrO$_x$-800	240	22.1	0.4
EP-WZrO$_x$-900	179	18.2	0.54
EP-WZrO$_x$-1000	105	16.8	0.92
WZrO$_x$-800	58	5.9	7.8
WZrO$_x$-900	28	7.9	16.4
WZrO$_x$-1000	2.8	/	158.3

Table S2: F-C reaction of Anisole and alcohol.[a]

Entry	Alcohol	Conversion(%)
1	4-Methylbenzyl alcohol	100
2	4-Methoxybenzyl alcohol	100
3	4-chlorobenzyl alcohol	20
4	2-Phenylethyl alcohol	<1
5	3-Phenylpropanol	<1

[a] Reaction conditions: Anisole (50 mmol), Alcohol (5 mmol), Cat. (EP-WZrO$_x$-1000, 50 mg), 1 h, 120 ^{o}C

Fig. S1 : The active energy of EP-$WZrO_x$-800, EP-$WZrO_x$-1000 and $WZrO_x$-800.[a]



[a] Reaction conditions: Anisole (50 mmol), Benzyl alcohol (5 mmol), 0.5 h
m (cat.) = 50 mg.

Fig. S2: Py-IR spectra of EP-WZrO$_x$-T. (B= Brönsted acid site，L= Lewis acid site)

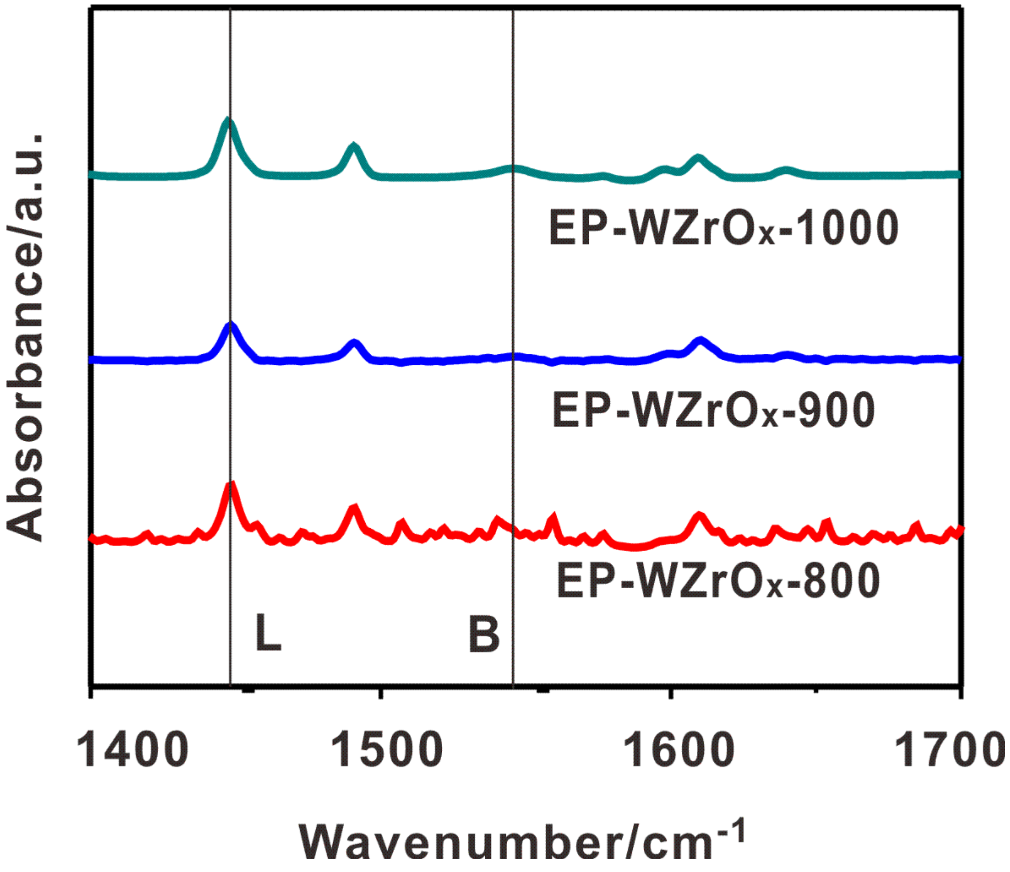


Fig. S3: Raman spectroscopy of WZrO$_x$-T and EP-WZrO$_x$-T. m-WO$_3$ (black circle). The Raman bands appeared at 810,750 and 270 cm^{-1} corresponds to the formation of m-WO$_3$ crystal.