Electronic Supplementary Material (ESI) for Green Chemistry.

Catalytic Conversion of Ethanol to Butadiene over High Performance LiZnHf-MFI Zeolite Nanosheets

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Experimental

1.1. Materials

Ethanol (EtOH, 99.7%, Sinopharm), tetraethyl orthosilicate (TEOS, 98%, Aldrich), $Zn(NO_3)_2 \cdot 6H_2O$ (99%, Aldrich), $HfCl_4$ (99.9%, Aldrich), and tetrapropylammonium hydroxide (TPAOH, 2.0 mol/L in H_2O, Aldrich), Tetrabutylphosphonium hydroxide solution (TBPOH, 40 wt. % in H_2O, Aladdin), and Li_2CO_3 (99.9%, Aldrich) were used as received without further purification.

1.2. Catalyst Preparation

Synthesis of MFI zeolite nanosheets Synthesis of MFI zeolite nanosheets was performed according to a previously reported procedure.[1] In a typical synthesis of a zeolite nanosheet, TBPOH was added dropwise into tetraethyl orthosilicate while stirring. Deionized water was then added to the mixture. The mixture was stirred for 12 h, and a clear sol with composition $1SiO_2$: 0.3TBPOH: $10H_2O$: 4EtOH was formed. The sol was sealed in a Teflon-lined stainless steel autoclave and heated for 40 h in a pre-heated oven operating at 388 K. Then, the precipitated white powder was collected by filtration and dried at 373 K. The dried sample was calcined at 823 K for 4 h to remove the organics.

Synthesis of microporous Hf-MFI zeolite Hf-MFI was prepared as follows: $HfCl_4$ was added to deionized water in a beaker, and then TEOS and TPAOH was added under continuous stirring, finally the mixture was stirred for 3 h. The molar composition of the synthesis gel was $0.024HfO_2$: $1.0SiO_2$: 0.5TPAOH: $30H_2O$. The gel was transferred to a PTFE-lined stainless steel autoclave and heated to 433 K for 48 h. Finally, the solid was repeatedly centrifuged and washed with deionized water, then dried at 373 K overnight. The solid was calcined at 823 K for 4 h to remove the organics.

Preparation of ZnHf-MFI and LiZnHf-MFI catalysts Zn and Hf were supported onto the MFI zeolite nanosheets (1.0 g) by wet-impregnation methods using $Zn(NO_3)_2 \cdot 6H_2O$ (0.07 g) and $HfCl_4$ (0.18 g) solution followed by drying at 353 K and calcination at 823 K for 4 h. The resultant catalyst was denoted as ZnHf-MFI(NS). LiZnHf-MFI(NS) was prepared by wet-impregnation of Li_2CO_3, $Zn(NO_3)_2 \cdot 6H_2O$ and $HfCl_4$ onto the MFI zeolite nanosheets. ZnHf-MFI(M) and LiZnHf-MFI(M) were also prepared by wet-impregnation of the corresponding metal precursors onto the microporous Hf-MFI, and dried at 353 K and calcined at 823 K for 4 h. Elemental analysis confirmed the Zn and Hf content within 1.4-1.6 wt% and 8.7-9.2 wt%, respectively.

Synthesis of ZnHf-S-1 catalyst S-1 was prepared by a gel with a molar composition of $1.0SiO_2$: 0.2TPAOH: $46H_2O$. The gel was transferred to a PTFE-lined stainless steel autoclave and heated to 443 K for 72 h. Finally, the solid was washed with deionized water, dried at 373 K and calcined at 823 K for 4 h to remove the organics. ZnHf-S-1 was prepared by wet-impregnation of the corresponding metal precursors onto the S-1 zeolite.

1.3. Catalyst Characterization

X-ray diffraction (XRD) patterns were recorded with a PANalytical X'Pert-Pro powder X-ray diffractometer, using Cu-Kα monochromated radiation ($\lambda = 0.1541$ nm) at a scanning speed of 5°/min in the range 5-50°. The crystal morphology was observed by scanning electron microscopy (SEM) using a JSM-7800F. Transmission electron microscopy (TEM) images and energy-dispersive X-ray spectroscopy (EDS) elemental mapping were performed using a JEM-2100F microscope, operated at a voltage of 200 kV. N_2 adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2460 system. The total surface area was calculated based on the BET equation. The micropore volume was evaluated using the t-plot method. Mesopore volume and external surface area were evaluated from the adsorption isotherm by the Barrett-Joyner-Halenda (BJH) method. The pyridine-adsorbed IR spectra were carried out on a Bruker Tensor 27 instrument. The calcined samples were dehydrated at 673 K for 1 h under a vacuum of 1.0×10^{-2} Pa, and then pyridine vapor was adsorbed at room temperature for 30 s. After reaching equilibrium, the pyridine-adsorbed system was evacuated at 423 K, 523 K and 623 K. The IR spectra were recorded at the corresponding temperatures, respectively. Thermogravimetric analysis (TG) was performed on a TA SDTQ600 analyzer with a temperature-programmed rate of 10 K min^{-1} in air. The retained organics in the spent catalyst after the ETB reaction were analyzed by GC-MS. The spent catalyst was dissolved with a HF solution (20 wt%), and then the organic compounds present in them were extracted by using CH_2Cl_2 and analyzed by a gas chromatograph equipped with a FID detector and a mass sensitive detector (Agilent 7890A/5975C) using a capillary column of HP-5.

1.4. Catalytic Reactions

Catalytic experiments were performed in a flow-type fixed-bed reactor under atmospheric pressure. In a typical experiment, 1.0 g calcined catalyst was loaded in the stainless steel tubular reactor and activated at 673 K in a nitrogen flow of 40 ml/min for 30 min before starting each reaction run, and then the temperature was adjusted to a reaction temperature of 593 K. Ethanol was used as a feed, and the weight hourly space velocity (WHSV) was 0.47 h^{-1}. The reaction mixture was fed using a syringe pump. The reaction products were analyzed using an online gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and HP-PLOT Q Column. The ethanol conversion and product selectivity were calculated as:
Conversion (%) = Moles of ethanol reacted / Moles of ethanol fed to the reactor× 100,
Selectivity (%) = Moles of carbon in the target product / Moles of carbon in ethanol reacted × 100.

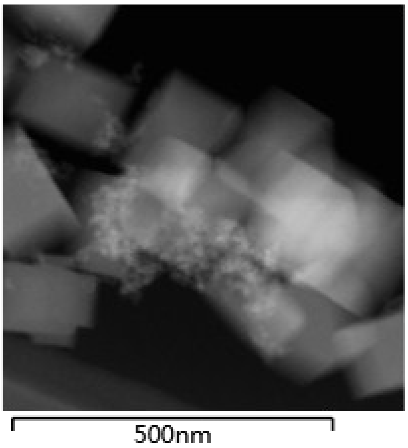

Fig.S1 TEM image of ZnHf-S-1.

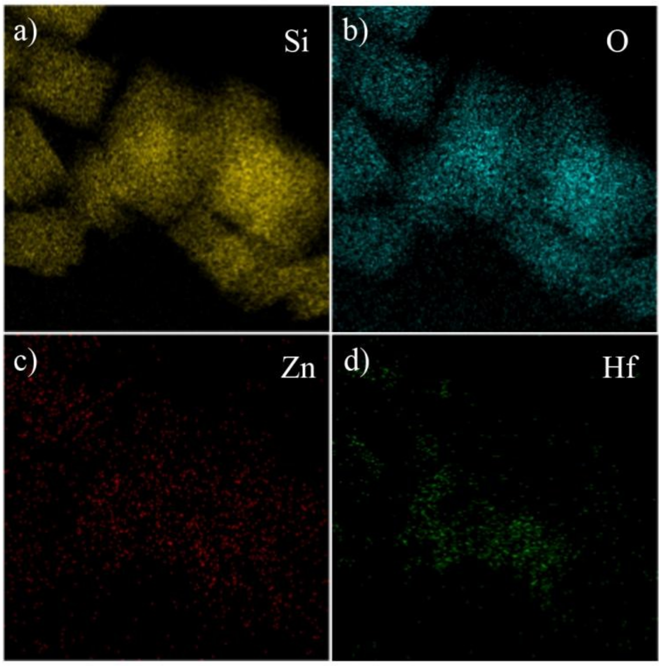

Fig.S2 EDS elemental mapping of ZnHf-S-1.

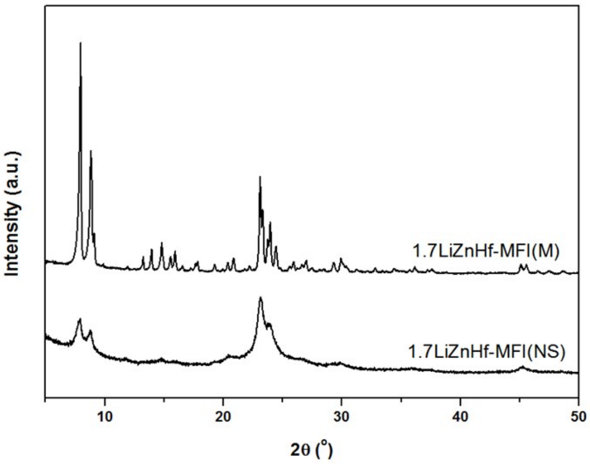

Fig.S3 XRD patterns of catalysts 1.7LiZnHf-MFI(M) and 1.7LiZnHf-MFI(NS).

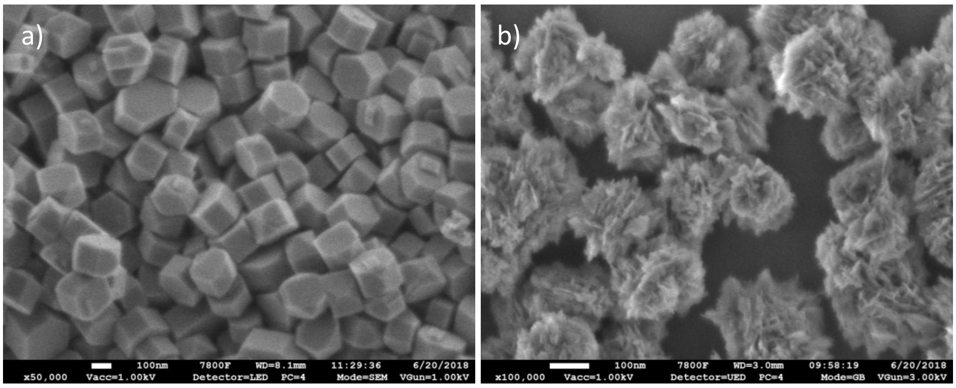

Fig.S4 SEM of catalysts 1.7LiZnHf-MFI(M) (a) and 1.7LiZnHf-MFI(NS) (b).

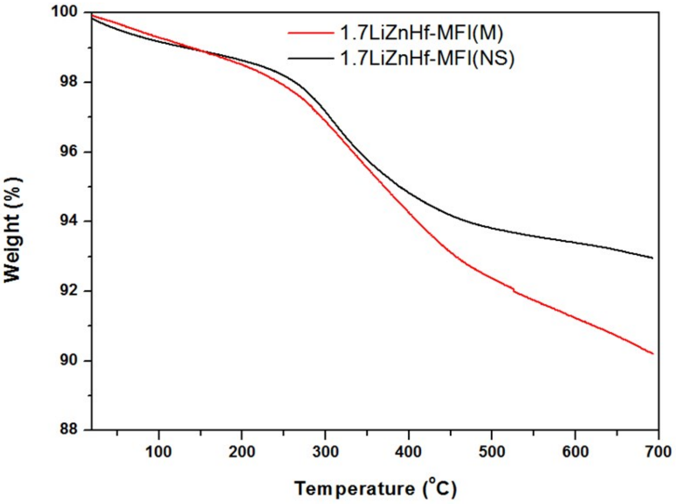

Fig.S5 TG curves of spent 1.7LiZnHf-MFI(M) and 1.7LiZnHf-MFI(NS) catalysts.

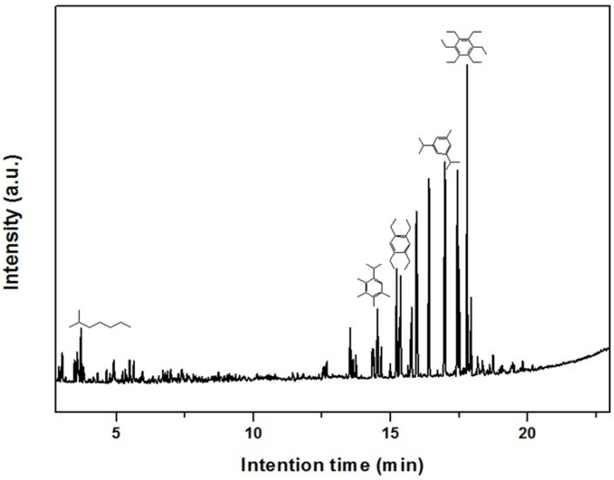

Fig. S6 GC-MS chromatograms of occluded organic species retained in spent 1.7LiZnHf-MFI (NS). The molecular structural formulas annotated on the chromatograms are identified by comparison with the mass spectra of those in the NIST database. (The spent catalyst was dissolved with a HF solution, and then the organic compounds present in them were extracted by using CH_2Cl_2 and analyzed by GC-MS.)

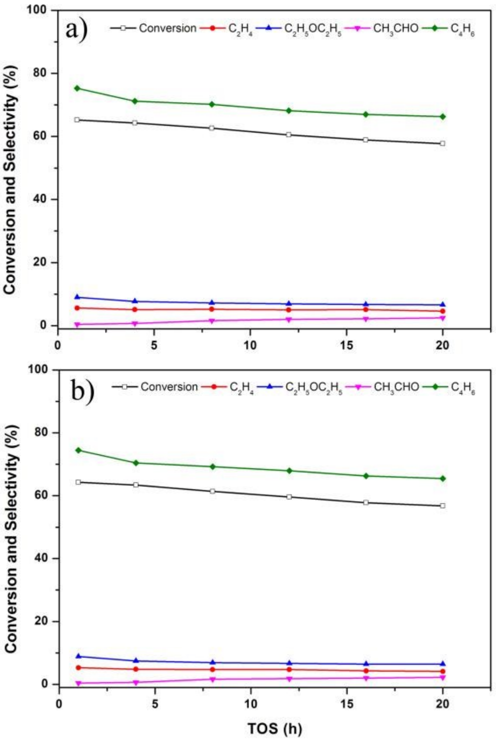

Fig.S7 Catalytic performances of 1.7LiZnHf-MFI(NS) in reaction cycle 2 (a) and cycle 3 (b) (T: 593 K, WHSV: 0.47 h^{-1}).

Table S1 Textural properties of the ZnHf-MFI catalysts.

Catalyst	S_{BET}[a](m^2g^{-1})	S_{Ext}[b](m^2g^{-1})	V_{micro}[c](cm^3g^{-1})	V_{meso}[b](cm^3g^{-1})	Pore size[d] (nm)
ZnHf-MFI(M)	367	69	0.17	0.22	-
ZnHf-MFI(NS)	413	232	0.09	0.32	4.3
1.7LiZnHf-MFI(M)	352	64	0.17	0.21	-
1.7LiZnHf-MFI(NS)	398	227	0.09	0.32	4.3
Spent 1.7LiZnHf-MFI(M)	242	23	0.13	0.05	-
Spent 1.7LiZnHf-MFI(NS)	314	188	0.07	0.21	4.2

[a] Total surface area is determined using the BET equation. [b] External surface area and mesopore volume are determined from the adsorption isotherm by the BJH method. [c] Micropore volume is determined by the t-plot method. [d] Pore size distribution is determined from the adsorption isotherm by the BJH method.

Table S2 Catalytic performance of the ZnHf-S-1 catalyst in the ethanol conversion to butadiene reaction after 3 h.

Catalyst	Conversion (%)	Product Selectivity (mol %)					
		Ethylene	Propylene	Butylene	Butadiene	Acetaldehyde	Diethyl ether
ZnHf-S-1	38.0	1.7	1.0	0.3	16.5	16.8	2.1

Table S3 Catalytic performance of the MFI supported catalysts in the ETB conversion after 3 h (T = 593 K, WHSV = 0.47 h^{-1}).

Entry	Catalyst	Conversion (%)	Product Selectivity (mol %)					
			Ethylene	Propylene	Butylene	Butadiene	Acetaldehyde	Diethyl ether
1	Zn-MFI	52.0	8.2	2.0	1.4	29.3	1.0	16.5
2	Hf-MFI	65.1	8.3	0	0	0.5	0	91.1
3	Hf-MFI*	63.4	8.2	0.5	0.8	26.1	0.7	49.1
4	ZnHf-MFI	63.6	11.1	2.9	1.5	43.0	1.1	24.3

*A mixture of 90 wt% ethanol and 10 wt% acetaldehyde was used as reactants.

Table S4 Catalytic performance of the MFI supported catalysts in the ETB reaction after 3 h (T = 593 K, WHSV = 0.47 h^{-1}).

Catalyst	Conversion (%)	Product Selectivity (mol %)					
		Ethylene	Propylene	Butylene	Butadiene	Acetaldehyde	Diethyl ether
1.7LiZnHf-MFI(NS)	64.6	5.3	2.3	1.8	73.0	0	12.6
1.7NaZnHf-MFI(NS)	54.2	2.3	1.2	1.0	45.2	3.2	7.3
1.7KZnHf-MFI(NS)	35.6	1.2	0.6	0.5	32.1	5.6	5.4

Literature

1. X. Y. Zhang, D. X. Liu, D. D. Xu, S. Asahina, K. A. Cychosz, K. V. Agrawal, A. Bhan, S. A. Hashimi, O. Terasaki, M. Thommes and M. Tsapatsis, *Science*, 2012, **336**, 1684.