Supplementary Material

Table S1. Summary of the preparation perspectives of hierarchical zeolite catalysts.

Catalyst	Method	Chemical	Condition
ZSM-5 nanosheets [1]	simple hydrothermal process	tetrabutylphosphonium hydroxide (TBPOH), tetraethyl orthosilicate (TEOS), aluminium isopropoxide, and sodium hydroxide (NaOH)	aging at ambient temperature for 12 hours, hydrothermal treatment at 130 °C for 2 days
nanospherical ZSM-5 nanosheets [2]	one-pot hydrothermal process	aluminosilicate (AS) nanobeads, tetrabutylammonium hydroxide (TBAOH), NaOH	stirring at room temperature for 12 hours, crystallization at 150 °C for 2 days
mesoporous ZSM-5 [3]	hydrothermal process	dimethyl octadecyl [3-(trimethoxysilyl)propyl] ammonium chloride (TPOAC) or hexadecyl trimethyl ammonium bromide (CTAB), tetrapropyl ammonium bromide (TPABr), colloidal silica (Ludox), sodium aluminate ($NaAlO_2$), NaOH, and sulfuric acid (H_2SO_4)	stirring for 4 hours, crystallization at 180 °C for 2 days
uniform mesoporous ZSM-5 [4]	hydrothermal process	tetrapropyl ammonium hydroxide (TPAOH), fumed silica, $NaAlO_2$, CTAB,	hydrothermal treatment at 150 °C for 2 days
hierarchical ZSM-5 [5]	hydrothermal process	sodium chloride (NaCl), aluminium isopropoxide, TPAOH, TEOS, and carbon black template	solvent evaporation at 90 °C, hydrothermal treatment at 180 °C for 3 days
ultrathin ZSM-5 [5]	hydrothermal process	quaternary ammonium surfactant of $C_8H_{17}–N^+(CH_3)_2–C_6H_{12}–N^+(CH_3)_2–C_8H_{17}$, LUDOX HS-40, and aluminium sulfate octadecahydrate	crystallization at 130 °C for 6 days under stirring condition
nanosized ZSM-5 [6]	dry gel method with steam-assisted hydrothermal condition	hexadecyltrimethoxysilane (HTS), TEOS, aluminum tritertbutoxide (ATTB), TPAOH, and ethanol as solvent	stirring for 1 hour before the solvent evaporation, crystallization at 180 °C for 5 days
nanosized BEA [7]	normal hydrothermal process	tetraethylammonium hydroxide (TEAOH), aluminum isopropoxide, NaOH, and silica powder resulting from the lyophilization of colloidal silica (Ludox AS-40)	hydrothermal treatment at 95 °C for 9 days
nano-sponge BEA [7]	hydrothermal process	poly-quaternary ammonium surfactant, ethanol, NaOH, $NaAlO_2$, and TEOS	stirring at 60 °C for 6 hours, crystallization at 140 °C for 4 days under tumbling condition
nanosized CHA [8]	hydrothermal conversion of FAU zeolite	*N*,*N*,*N*-trimethyl-1-adamantammonium hydroxide (TMAdaOH), dealuminated FAU powder, NaOH, and calcined CHA seed	hydrothermal treatment at 125-170 °C for 3 hours to 21 days

Table S1. (Continued) Summary of the preparation perspectives of hierarchical zeolite catalysts.

Catalyst	Method	Chemical	Condition
ZSM-5 [9]	desilication	0.2 M NaOH solution	vigorous stirring at 65 °C for 30 min
ZSM-5 [10]	dealumination	0.5 M of oxalic acid aqueous solution	at 120 °C for 2 hours
ZSM-5 [11]	sequential desilication and dealumination	0.2 M NaOH, 0.5 M oxalic acid	stirring at 65 °C for 30 min (desilication), heating at 120 °C for 2 hours (dealumination)
zeolite L [12]	sequential desilication and dealumination	0.8 M of NaOH, 0.2 M of HNO_3	at 65 and 80 °C for 2 hours (desilication), at 65 °C for 2 hours (dealumination)
zeolite L [12]	sequential dealumination and desilication	0.2 M or 0.3 M of HNO_3, 0.1 M of NaOH	at 65 °C for 2 hours (dealumination), at 65 °C for 30 min (desilication)
zeolite L [12]	sequential dealumination and desilication	0.2 M and 0.5 M NH_4Cl, 0.1 M of NaOH	at 80 °C for 1 hour (dealumination)
zeolite L [12]	sequential dealumination and desilication	water steaming, 0.8 M NaOH	steaming at 550 or 600 °C with 1.8 ml/min of continuous liquid water flow for 3 hours (dealumination), at 80 °C for 2 hours (desilication)
hierarchical ZSM-5 [13]	steam treatment	water steaming	at 400, 450, 500, to 550 °C for 6 hours with 13.8 h^{-1} of WHSV in the fixed-bed flow reactor
hierarchical ZSM-5 [5]	alkaline treatment	NaOH and tetrabutylammonium hydroxide (TBAOH) mixture solution	at 80 °C for 5 hours
hierarchical MFI-type zeolite [14]	ultrasonic-assisted desilication	mixed solution of NaOH and TBAOH	ultrasound condition with 600 W of power and 20 kHz of frequency, treatment at low temperature for 30 min
mesoporous BEA [15]	desilication	0.2 M NaOH, 0.003 M $Al(NO_3)_3$, and 0.1 M TPAOH	at 313 K for 30 min
mesoporous BEA [15]	desilication	0.1 M NaOH	at 313 K for 10 min
mesoporous BEA [15]	desilication	0.1 M NaOH, 0.003 M $Al(NO_3)_3$, and 0.02 M TMAOH	at 338 K for 30 min
mesoporous BEA [15]	desilication	0.003 M $Al(NO_3)_3$ and 0.1 M TPAOH	at 313 K for 30 min

Table S1. (Continued) Summary of the preparation perspectives of hierarchical zeolite catalysts.

Catalyst	Method	Chemical	Condition
mesoporous BEA [16]	surfactant-template treatment	NaOH and decyltrimethylammonium bromide (DTAB-10) or dodecyltrimethylammonium bromide (DTAB-12) or tetradecyltrimethylammonium bromide (TTAB) or cetyltrimethylammonium bromide (CTAB)	stirring at room temperature for 30 min, hydrothermal treatment at 80-140 °C for 1-24 hours
mosaic mesoporous ZSM-5 [17]	fluoride etching	40 wt.% of NH_4F aqueous solution	stirring at 50 °C for 60 min under ultrasonication
house-of-cards-like ZSM-5 [18]	fluoride etching	40 wt.% of NH_4F aqueous solution	at 50 °C for 60 min under mechanical stirring and ultrasonication
pore-opened MOR [19]	fluoride etching	20 wt.% of NH_4F aqueous solution	stirring at 50 °C for 2 hours
chromosilicate ZSM-5 [20]	hydrothermal	silicic acid, chromium(III) nitrate, sodium carbonate or potassium carbonate or cesium carbonate, sulfuric acid, and TPABr	vigorous stirring at room temperature for about 4 hours, hydrothermal treatment at 155 °C for 100 hours
alkali metal modified ZSM-5 [21]	alkali metal cations modification	$LiNO_3$, $NaNO_3$, KNO_3 and $CsNO_3$	ion-exchange at 25 °C for 30 min under 200 rpm
Cs-ZSM-5 [22]	wet impregnation	0.01 M solution of cesium nitrate	vigorous stirring at 80 °C for 2 hours
ceria incorporated hierarchical MFI zeolite [23]	ion-exchange	cerium(III) acetate aqueous solution	at 80 °C for 2 hours
ceria supported hierarchical MFI zeolite [23]	impregnation	cerium(III) acetate aqueous solution	at room temperature for 24 hours
WO_x nanoparticles supported on MFI zeolite nanosheets [24]	incipient wetness impregnation	ammonium metatungstate hydrate solution	zeolite dispersing into the solution for 2 hours
vanadium (V) or lanthanum (La) or titanium (Ti) incorporated ZSM-5 and FER zeolites [25]	incipient wetness impregnation	ammonium vanadate (NH_4VO_3) and hydrogen peroxide (H_2O_2), aqueous solution of lanthanum nitrate hexahydrate ($La(NO_3)_3{\cdot}6H_2O$), titanium isopropoxide dissolved in isopropanol	-

Table S1. (Continued) Summary of the preparation perspectives of hierarchical zeolite catalysts.

Catalyst	Method	Chemical	Condition
5wt.%Ni-ZSM-5 [26]	wet incipient	aqueous solution of $Ni(NO_3)\cdot 6H_2O$	mixing the ZSM-5 zeolite and the Ni solution for a while
1wt.%Ni-ZSM-5 [27]	incipient wetness	aqueous solution of $Ni(NO_3)\cdot 6H_2O$	slow dropping the Ni solution on the ZSM-5 powder
Ni loaded on BEA zeolite [28]	sol gel impregnation	$Ni(NO_3)_3\cdot 6H_2O$ and citric acid in deionized water	treatment at 60 °C for 12 hours
cobalt (Co) supported on mesoporous Y zeolite [29]	incipient wetness impregnation	aqueous solution of cobalt(II) nitrate	-
bimetallic InV-ZSM-5 [30]	ion-exchange under reflux condition	0.05 M of vanadium(III) chloride aqueous solution, 0.015 M of indium(III) nitrate aqueous solution	1. V loading: at 80 °C for 16 hours 2. In loading: at 80 °C for 16 hours
MoZn/$AlPO_4$-5 [31]	incipient wetness impregnation	aqueous solution of ammonium molybdate and zinc acetate	-
Ag-promoted Zr-BEA [32]	stepwise metal incorporation	$ZrOCl_2\cdot 8H_2O$ solution in DMSO solvent, $AgNO_3$ solution	1. Zr loading: heated at 403 K for 12 hours 2. Ag doping: incipient wetness impregnation
Mg-ZrO_x/MFI nanosheet [33]	incipient wetness impregnation	zirconium oxynitrate aqueous solution, magnesium nitrate solution	1. Zr impregnation 2. Mg impregnation
Ag- or Cu- or Zn-Ta/ Si-rich-BEA [34]	stepwise metal incorporation	solution of $Ta(OC_2H_5)_5$ in isopropanol, $AgNO_3$ or $Cu(NO_3)_2\cdot 3H_2O$ or $Zn(NO_3)_2\cdot 6H_2O$ aqueous solutions	1. Ta loading: stirring at 353 K for 3 hours 2. Ag or Cu or Zn loading: stirring at 298 K for 2 hours
LiZnHf-MFI nanosheet [35]	wet impregnation	solutions of Li_2CO_3, $Zn(NO_3)_2\cdot 6H_2O$, and $HfCl_4$	-
Cs-Fe-Mo/ZSM-5 [36]	three-step impregnation	aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, $Fe(NO_3)_3\cdot 9H_2O$, and $CsNO_3$	1. Mo loading: vigorous stirring (500 rpm) at 80 °C for 2 hours 2. Fe adding: stirring for another 2 hours 3. Cs adding: stirring for another 2 hours
trimetallic Zn-promoted Cu-Ni alloy supported on ZSM-5 [37]	one-step impregnation	mixed solution of $Cu(NO_3)_2\cdot 2.5H_2O$, $Zn(NO_3)_2\cdot 6H_2O$, and $Ni(NO_3)_2\cdot 6H_2O$	preparation of mixed metal solution by stirring at 35 °C for 4 hours and subsequent adding of ZSM-5 powder under stirring

Table S1. (Continued) Summary of the preparation perspectives of hierarchical zeolite catalysts.

Catalyst	Method	Chemical	Condition
bimetallic V-Cu/ZSM-5 [38]	incipient wetness impregnation	ammonium metavanadate (NH_4VO_3) and copper nitrate hydrate ($Cu(NO_3)_2{\cdot}xH_2O$)	-
Cu-SSZ-13 [39]	one-pot synthesis	Cu-tetraethylenepentamine (Cu-TEPA) complex from $CuSO_4{\cdot}5H_2O$ and TEPA, $NaAlO_2$, silica sol, and NaOH	aging for 3 hours, hydrothermal heating at 140 °C for 4 days
Sn- or Ge- or Zr-MFI nanosheet [40]	isomorphous substitution	TEOS, germanium oxide or zirconyl(IV) nitrate or tin(IV) chloride pentahydrate, TBAOH, and NaOH	stirring for 12 hours, hydrothermal treatment at 130 °C for 2 days

Table S2. Characterization of hierarchical zeolite catalysts.

Catalyst	Properties	Characterization technique	Results
ZSM-5 zeolites before and after desilication [9]	textural properties	N_2-adsorption-desorption	parent ZSM-5: type I isotherm, $S_{external}$ = 61 m^2/g, $V_{mesopore}$ = 0.07 cm^3/g desilicated ZSM-5: type IV isotherm, $S_{external}$ = 212 m^2/g, $V_{mesopore}$ = 0.37 cm^3/g
hierarchical nanosheet and microporous MFI zeolites [35]	morphology and porous structure	scanning electron microscope (SEM) and transmission electron micros-copy (TEM)	microporous MFI: bulk hexagonal crystal morphology with 500 nm of particle size hierarchical MFI nanosheet: 200 nm of uniform spherically-shaped crystals with rough surface of stacked nanosheets, 2-10 nm of sheet thickness, and intracrystalline mesopores between nanosheets
bulk and nanosheet MFI zeolites [35]	textural properties	N_2-adsorption-desorption	nanosheet MFI zeolite: $S_{external}$ = 232 m^2/g, $V_{mesopore}$ = 0.35 cm^3/g bulk MFI zeolite: $S_{external}$ = 69 m^2/g, $V_{mesopore}$ = 0.22 cm^3/g
desilicated, NH_4F treated, nanosheet ZSM-5 zeolites [18]	textural properties	N_2-adsorption-desorption	desilicated ZSM-5: S_{BET} = 494 m^2/g, S_{ext} = 206 m^2/g, V_{mic} = 0.13 cm^3/g, V_{meso} = 0.36 cm^3/g NH_4F treated ZSM-5: S_{BET} = 395 m^2/g, S_{ext} = 54 m^2/g, V_{mic} = 0.17 cm^3/g, V_{meso} = 0.31 cm^3/g nanosheet ZSM-5: S_{BET} = 504 m^2/g, S_{ext} = 266 m^2/g, V_{mic} = 0.11 cm^3/g, V_{meso} = 0.40 cm^3/g

Table S2. (Continued) Characterization of hierarchical zeolite catalysts.

Catalyst	Properties	Characterization technique	Results
hierarchical BEA zeolites prepared by treatment with various surfactants [16]	textural properties	N_2-physisorption	DTAB-10: S_{BET} = 495 m^2/g, S_{micro} = 332 m^2/g, S_{meso} = 163 m^2/g, V_{total} = 0.386 cm^3/g, V_{micro} = 0.175 cm^3/g, V_{meso} = 0.211 cm^3/g DTAB-12: S_{BET} = 541 m^2/g, S_{micro} = 327 m^2/g, S_{meso} = 214 m^2/g, V_{total} = 0.412 cm^3/g, V_{micro} = 0.169 cm^3/g, V_{meso} = 0.243 cm^3/g TTAB: S_{BET} = 540 m^2/g, S_{micro} = 332 m^2/g, S_{meso} = 208 m^2/g, V_{total} = 0.403 cm^3/g, V_{micro} = 0.172 cm^3/g, V_{meso} = 0.231 cm^3/g CTAB: S_{BET} = 519 m^2/g, S_{micro} = 315 m^2/g, S_{meso} = 208 m^2/g, V_{total} = 0.422 cm^3/g, V_{micro} = 0.164 cm^3/g, V_{meso} = 0.258 cm^3/g
micron-sized (MC), nanometer-sized (NC), and nano-sponge (NS) BEA zeolites [7]	morphology and porous structure	SEM and TEM	MC BEA: bulk bipyramidal morphology NC BEA: random aggregation of nanocrystals with intercrystalline mesopores NS BEA: sponge-like morphology with ordered mesopores
micron-sized (MC), nanometer-sized (NC), and nano-sponge (NS) BEA zeolites [7]	textural properties	N_2-physisorption	MC BEA: S_{BET} = 626 m^2/g, S_{ext} = 33 m^2/g, V_{micro} = 0.23 cm^3/g, V_{meso} = 0.05 m^3/g NC BEA: S_{BET} = 726 m^2/g, S_{ext} = 223 m^2/g, V_{micro} = 0.24 cm^3/g, V_{meso} = 0.71 m^3/g NS BEA: S_{BET} = 977 m^2/g, S_{ext} = 185 m^2/g, V_{micro} = 0.30 cm^3/g, V_{meso} = 0.74 m^3/g
pure silica MFI zeolite nanosheets before and after the incorporation of tungsten oxide (WO_x) nanoparticle [24]	textural properties	N_2-physisorption	pristine MFI: S_{BET} = 642 m^2/g, S_{micro} = 152 m^2/g, S_{ext} = 489 m^2/g, V_{total} = 0.71 cm^3/g 2mol%WO_x-MFI: S_{BET} = 470 m^2/g, S_{micro} = 153 m^2/g, S_{ext} = 317 m^2/g, V_{total} = 0.577 cm^3/g 6mol%WO_x-MFI: S_{BET} = 396 m^2/g, S_{micro} = 128 m^2/g, S_{ext} = 267 m^2/g, V_{total} = 0.49 cm^3/g
microporous, desilicated, mesoporous, carbon-black templated, and ultrathin ZSM-5 zeolites [5]	porosities	quasi-equilibrated temperature programmed desorption and adsorption (QE-TPDA) of *n*-nonane (nC_9)	microporous ZSM-5: V_{micro} = 0.17 cm^3/g, V_{meso} = 0.09 cm^3/g desilicated ZSM-5: V_{micro} = 0.15 cm^3/g, V_{meso} = 0.37 cm^3/g mesoporous ZSM-5: V_{micro} = 0.14 cm^3/g, V_{meso} = 0.43 cm^3/g carbon-templated ZSM-5: V_{micro} = 0.16 cm^3/g, V_{meso} = 0.09 cm^3/g ultrathin ZSM-5: V_{micro} = 0.12 cm^3/g, V_{meso} = 0.20 cm^3/g

Table S2. (Continued) Characterization of hierarchical zeolite catalysts.

Catalyst	Properties	Characterization technique	Results
MOR zeolites before and after NH_4F etching [19]	pore architecture in 3-dimensional view	electron tomography (ET) with the tilting angles from -70° to +70°	parent MOR: small amount of closed mesopores inside the zeolite crystal NH_4F treated MOR: opened-porous structure with the pore network connectivity from the external surface into the internal zeolite crystal
zeolite Y catalysts before and after the acid modification with phosphoric acid [41]	acidic properties	temperature programmed desorption of ammonia (NH_3-TPD)	total number of acid sites: 12.3 mmol/g of parent Y zeolite, 3.4, 4.7, and 6.0 mmol/g of 10, 20, and 30 wt.% H_3PO_4 modified Y zeolites
ZSM-5 zeolites before and after steam treatment [13]	acidic properties	NH_3-TPD	The steam treated ZSM-5 displayed lower acid strength compared to the parent one.
isolated ZSM-5 zeolite and hierarchical ZSM-5@Silicalite-1 nanosheet composite [42]	acidic properties	NH_3-TPD	isolated ZSM-5 zeolite: 0.966 mmol/g of total acidity hierarchical ZSM-5@Silicalite-1 nanosheet composite: 0.184 mmol/g of total acidity
Li, Zn, and Hf incorporated microporous (M) and nanosheet (NS) MFI zeolites [35]	qualitative and quantitative analysis of Brønsted and Lewis acid sites	Fourier transform infrared spectroscopy (FTIR) of pyridine adsorption	number of Lewis acid sites (LAS): ZnHf-MFI(M) = 18 μmol/g, ZnHf-MFI(NS) = 36 μmol/g, LiZnHf-MFI(NS) = 32 μmol/g, LiZnHf-MFI(M) = 14 μmol/g
microporous, desilicated, mesoporous, carbon-black templated, and ultrathin ZSM-5 zeolites [5]	accessibility of acid sites	FTIR of 2,6-di-*tert*-butylpyridine (dTBPy) and pivalonitrile (Pn) adsorption	accessibility factors for 2,6-di-*tert*-butylpyridine (AF_{dTBPy}) and pivalonitrile (AF_{Pn}) microporous ZSM-5: AF_{dTBPy} = 0.04, AF_{Pn} = 0.12 desilicated ZSM-5: AF_{dTBPy} = 0.24, AF_{Pn} = 0.41 mesoporous ZSM-5: AF_{dTBPy} = 0.49, AF_{Pn} = 0.51 carbon-black templated ZSM-5: AF_{dTBPy} = 0.04, AF_{Pn} = 0.10 ultrathin ZSM-5: AF_{dTBPy} = 0.45, AF_{Pn} = 0.73
Zr incorporated dealuminated BEA catalysts [43]	acidities	FTIR of CO adsorption	area of band centered at 2228 cm^{-1} (Al^{3+} Lewis acid sites), 2174 cm^{-1} (Brønsted acid sites), and 2188 cm^{-1} (Zr^{4+} Lewis sites) 1.3 wt.% Zr-BEA: < 0.002, 0.06, and 0.99 2.1 wt.% Zr-BEA: < 0.002, 0.07, and 1.50 3.3 wt.% Zr-BEA: < 0.002, 0.07, and 2.36 3.5 wt.% Zr-BEA: < 0.002, 0.11, and 2.49

Table S2. (Continued) Characterization of hierarchical zeolite catalysts.

Catalyst	Properties	Characterization technique	Results
Ta-BEA and MTa-BEA catalysts where M is Ag, Cu, or Zn [34]	basic properties	FTIR of pyrrole and $CDCl_3$ adsorption	Pyrrole: The shoulder band at 3390 cm^{-1} was found in all BEA catalysts indicating the presence of weak basic sites. $CDCl_3$: The Ta-BEA sample showed the bands at 2258 and 2224 cm^{-1} which are assigned to weak and medium basic sites, respectively. The MTa-BEA catalysts presented only the band of weak basic sites at 2256 cm^{-1}.
MTa-BEA catalysts where M is Ag, Cu, or Zn [34]	metal species	X-ray photoelectron spectroscopy (XPS)	Ta $4f_{5/2}$ and $4f_{7/2}$ (29.1-29.2 and 24.8-25.2 eV): Ta(V) species with well dispersion on the zeolite surfaces Ag $3d_{3/2}$ and $3d_{5/2}$ (374.6 and 368.65 eV): Ag(I) species and oxidized silver clusters Cu $2p_{1/2}$ and $2p_{3/2}$ (953.3 and 933.3 eV): Cu(II) species with well dispersion and strong interaction with the BEA zeolite Zn $2p_{1/2}$ and $2p_{3/2}$ (1045.5 and 1022.5 eV): Zn(II) species dispersed in the zeolite structure
Zr supported on microporous and nanosheet MFI zeolites [33]	metal species	UV-vis diffuse reflectance spectroscopy	microporous MFI: the shoulder band at 230 nm of Zr-O-Zr linkages in nanoscopic regions MFI nanosheet: the highest absorbance edge energy of Zr indicating the best dispersion of Zr oxide both MFI supports: the blue shift from 230-240 nm of bulk ZrO_2 to 205-215 nm indicating the ligand-to-metal charge transfer (LMCT) from O^{2-} to isolated Zr^{4+} in the tetrahedral structure
Zr supported on microporous and nanosheet MFI zeolites [33]	metal species	Raman spectroscopy	the band at 637 cm^{-1}: the monoclinic ZrO_2 the bands at 550 and 476 cm^{-1}: the three-dimensional amorphous ZrO_2 MFI nanosheet: These bands showed very low intensity demonstrating the high dispersion of ZrO_2 without the formation of bulk ZrO_2 species.

Table S2. (Continued) Characterization of hierarchical zeolite catalysts.

Catalyst	Properties	Characterization technique	Results
Ce incorporated conventional and hierarchical ZSM-5 zeolites [23]	metal species	X-ray absorption near edge structure (XANES)	conventional ZSM-5: high fraction of Ce^{4+} species hierarchical ZSM-5: high fraction of Ce^{3+} species with highly dispersed and very small Ce particles
tungsten oxide (WO_x) supported on MFI nanosheet catalysts [24]	metal species	XANES and the Extended X-ray absorption fine structure (EXAFS)	XANES: an absorption band at 10,213 eV of the W^{6+} species in monoclinic WO_3 EXAFS: - 1.8 Å of bond distance between a tungsten atom and a nearest oxygen atom in the monoclinic WO_3 - The coordination number (CN) increased with the increasing of tungsten oxide content confirming the larger particle size of tungsten oxide in the higher loading sample.

Table S3. Catalytic behaviors of hierarchical zeolites in bioethanol conversion to monomers.

Reaction	Catalyst	Condition	Catalytic performance
Bioethanol dehydration	alkaline-acid treated zeolite L [12]	280 °C, atmospheric pressure, 1.7 h^{-1} of space velocity	99% of ethanol conversion and 96% of ethylene yield
	desilicated and dealuminated ZSM-5 zeolites [11]	200 °C, ambient pressure, 0.2 g of catalyst, 19.8 kPa of ethanol partial pressure in He	70-76% of ethanol conversion and ~5-17% of ethylene selectivity
	dealuminated ZSM-5 [10]	220 °C, 2.5 h^{-1} of WHSV, 95% of ethanol concentration	98.5% of ethylene yield and 100% of ethylene selectivity
	phosphorous modified ZSM-5 [10]	240 °C, 1.5 h^{-1} of WHSV, 20% of the ethanol concentration	94.3% of ethylene yield and 94.4% of ethylene selectivity
	10-30 wt.% of H_3PO_4 modified zeolite Y catalysts [41]	673 K, 4.6×10^4 h^{-1} of WHSV, 16 kPa of ethanol partial pressure	10wt.%H_3PO_4/Y zeolite: 98.3 of ethylene selectivity 20wt.%H_3PO_4/Y zeolite: 93.9 of ethylene selectivity 30wt.%H_3PO_4/Y zeolite: 96.5 of ethylene selectivity
	20 wt.% of NH_4F treated MOR zeolite [19]	400 °C, 0.2 g of catalyst, 2 g/h of ethanol with 2.5 M ratio of N_2/ethanol	approximately 80% of ethylene yield
	steam-treated ZSM-5 at 500 °C [13]	275 °C, atmospheric pressure, 1.0 g of catalyst, 2.37 h^{-1} of WHSV	98.6% of ethanol conversion and 98.5% of ethylene selectivity

Table S3. (Continued) Catalytic behaviors of hierarchical zeolites in bioethanol conversion to monomers.

Reaction	Catalyst	Condition	Catalytic performance
Bioethanol dehydration	nanoscale and microscale ZSM-5 catalysts [44]	240 °C, atmospheric pressure, 1 g of catalyst, 45(v)% of ethanol concentration, 0.8 h^{-1} of WHSV	nanoscale ZSM-5: 98.27% of ethanol conversion and 96.48% of ethylene selectivity at 260 h of TOS microscale ZSM-5: 92.92% of ethanol conversion and 93.00% of ethylene selectivity at 50 h of TOS
	microporous, desilicated, mesoporous, carbon-black templated, and ultrathin ZSM-5 zeolites [5]	240 °C, 0.05 g of catalyst, 1.1 $g_{ethanol}$ $g_{catalyst}^{-1}$ h^{-1} of space velocity	site time yield (STY, 10^{-2} g/s) microporous ZSM-5: STY_{DEE} = 1.92, STY_{C2} = 4.04 desilicated ZSM-5: STY_{DEE} = 1.78, STY_{C2} = 4.31 mesoporous ZSM-5: STY_{DEE} = 3.01, STY_{C2} = 0.85 carbon templated ZSM-5: STY_{DEE} = 0.11, STY_{C2} = 5.26 ultrathin ZSM-5: STY_{DEE} = 3.21, STY_{C2} = 1.41
	hierarchical SAPO-34@ZSM-5 and SAPO-34@silicalite-1 core-shell zeolite composites [45]	400 °C, atmospheric pressure, 0.5 g of catalyst, 1.5 mL h^{-1} of ethanol	SAPO-34@ZSM-5: 84.5% of ethanol conversion, ~65% of ethylene selectivity, ~15% of propylene selectivity, and ~80% of total light olefins selectivity SAPO-34@silicalite-1: 65.8% of ethanol conversion and ~99% of ethylene selectivity
	Ti loaded on dealuminated ZSM-5 zeolite [25]	280 °C, 1 g of catalyst, 7 h^{-1} of WHSV	96% of ethanol conversion and 88% of ethylene selectivity
	ceria incorporated hierarchical ZSM-5 nanosheet zeolite [23]	350 °C, 5 h^{-1} of $WHSV_{EtOH}$, 0.1 g of catalyst	yield of ethylene close to 100%
	WO_x nanoparticles supported on MFI zeolite nanosheets [24]	450 °C, 1.5 h^{-1} of WHSV, 100 mg of catalyst	ethylene selectivity decreased in the following order: 1mol%WO_x-MFI (92.86%) > 2mol%WO_x-MFI (92.54%) > 6mol%WO_x-MFI (92.44%) > 4mol%WO_x-MFI (91.07%)
	Cu-SSZ-13 zeolite [39]	212 °C, 1 atm of pressure, 1.63 h^{-1} of WHSV	higher than 99% of ethylene yield
	MoZn/$AlPO_4$-5 zeolite (Mo/Zn molar ratio = 4) [46]	400 °C, atmospheric pressure, 250 mg of catalyst, ethanol diluted in N_2 with flow rate of N_2 20 ml/min and isothermal saturator filled with ethanol at 20 °C	~87% of ethanol conversion and 93% of ethylene selectivity

Table S3. (Continued) Catalytic behaviors of hierarchical zeolites in bioethanol conversion to monomers.

Reaction	Catalyst	Condition	Catalytic performance
Bioethanol to hydrocarbons	HZSM-5 zeolite (Si/Al ratio of 15) [47]	300 °C, 320 °C, 360 °C, and 400 °C, ~4.7 h^{-1} of WHSV, 300 psig	- production amount of both paraffin and naphthene compounds: 300 °C > 320 °C > 360 °C > 400 °C - small amount of olefin production: 300 and 400 °C - no olefin production: 320 and 360 °C - production amount of benzene and xylene: 400 °C > 360 °C > 320 °C > 300 °C
	alkali-treated HZSM-5 zeolites with different Si/Al ratio [9]	360 °C, 15 bar, ~38 h^{-1}, and 3 h of TOS	low Si/Al ratio: more ethylene selective high Si/Al ratio: higher ethanol conversion and formation of heavier hydrocarbons
	fluorinated ZSM-5 catalysts [48]	500 °C, atmospheric pressure, ethanol/water = 9/1 vol/vol, and 10 h^{-1} of WHSV	100% ethanol conversion for all catalysts 5wt.%F-ZSM-5: 12.4% of ethylene, 16.4% of propylene, 9.7% of butylene, 37.5% of paraffins + aliphatics, 24.0% of aromatics 10wt.%F-ZSM-5: 17.5% of ethylene, 21.2% of propylene, 9.5% of butylene, 37.6% of paraffins + aliphatics, 14.1% of aromatics 15wt.%F-ZSM-5: 19.1% of ethylene, 21.5% of propylene, 9.6% of butylene, 33.1% of paraffins + aliphatics, 16.7% of aromatics 20wt.%F-ZSM-5: 21.9% of ethylene, 21.4% of propylene, 8.6% of butylene, 33.1% of paraffins + aliphatics, 15.0% of aromatics
	nano-sized and conventional ZSM-5 zeolites [6]	360 °C, 300 psig, 7.9 h^{-1} of WHSV	low Si/Al ratio samples (~40): lifetime of nano-sized ZSM-5 > conventional ZSM-5 approximately 2 times high Si/Al ratio zeolites (~140): lifetime of nano-sized ZSM-5 > conventional ZSM-5 approximately 5 times
	nanosized and conventional CHA zeolites [8]	400 °C, atmospheric pressure, total flow rate of 20 ml/min (C_2H_5OH/N_2 = 50/50 mol%)	100% of ethanol conversion for both catalysts nanosized CHA: 61.9% yield of C_2H_4 and 19.6% yield of C_3H_6 conventional CHA: 85.7% yield of C_2H_4 and 10.4% yield of C_3H_6

Table S3. (Continued) Catalytic behaviors of hierarchical zeolites in bioethanol conversion to monomers.

Reaction	Catalyst	Condition	Catalytic performance
Bioethanol to hydrocarbons	hierarchical mesoporous ZSM-5 synthesized using the HZSM-5 zeolite as a seed [4]	450 °C, 3 g of catalyst, atmospheric pressure, 2 ml/h of ethanol feed mixed with helium co-fed at 13.725 ml/min	mesoporous ZSM-5: - Ethylene was the main gas product and stable after 20 h of TOS. - a decrease in C_{10+} aromatic selectivity with an increase of TOS - much higher production content of large hydrocarbons including kerosene and gas oil HZSM-5: - a decrease in propane selectivity and an increase in ethylene, propylene, and mixed C_4 gas product selectivity - production of large hydrocarbons such as C_9 and C_{10+} aromatics after 96 h of TOS
	micron- and nanometer-size H-ZSM-5 zeolites [49]	623 K and 3.0 MPa of pressure	catalytic stability: nanometer-size H-ZSM-5 >> micron-size H-ZSM-5
	micron-sized, nanometer-sized, and nano-sponge BEA-type zeolites [7]	350 °C, 30 bar of total pressure, N_2/EtOH molar ratio = 4, gas hourly space velocity (GHSV) = 5.3 h^{-1}	complete ethanol conversion: nanosized and micron-sized BEA zeolites nano-sponge BEA: slightly lower ethanol conversion rate of catalyst deactivation: micron-sized >>> nanometer-sized > nano-sponge catalytic stability: nano-sponge > nanosized
	NH_4F treated, desilicated, and nanosheet ZSM-5 zeolites [18]	623 K, 3.0 MPa of total pressure, N_2/EtOH molar ratio = 4, gas hourly space velocity (GHSV) = 5.3 h^{-1}	parent ZSM-5: very low catalytic activity with only 35% of the initial C_{3+} yield and rapid catalyst deactivation desilicated ZSM-5: almost 100% of C_{3+} yield at the initial stage but fast catalyst deactivation nanosheet ZSM-5: lower initial C_{3+} yield but slower catalyst deactivation than desilicated ZSM-5 NH_4F treated ZSM-5: the highest catalytic stability with 60 mol% of C_{3+} yield after 90 hours of TOS
	Ni/HZSM-5 zeolite [50]	673 K, WHSV = 0.5, 1.8, and 3.5 h^{-1}	product distribution: high capability of aromatics and gaseous hydrocarbons production at lower WHSV ethanol conversion: stable at 90% during 168 hours of reaction time

Table S3. (Continued) Catalytic behaviors of hierarchical zeolites in bioethanol conversion to monomers.

Reaction	Catalyst	Condition	Catalytic performance
Bioethanol to hydrocarbons	bimetallic InV-ZSM-5 zeolite [51]	250-450 °C, 0.2 g of catalyst, 1.6 h^{-1} of WHSV	- higher yield of valuable C_{3+} products compared to the V-ZSM-5 and In-ZSM-5 zeolites - product distribution: 19% of C_3-C_4 olefins, 35% of C_3-C_4 paraffins, and 33% of C_{5+} liquid fractions - C_{5+} liquid fractions: 6.5% of olefins, 3.8% of paraffins, 24.0% of iso-paraffins, 5.4% of naphthenes, 60.2% of aromatics, and 4.2% of unidentified products
Bioethanol to butadiene	MgO impregnated on microporous and mesoporous LTA zeolites [15]	continuous two-step gas phase setup (0.400 g of CuO\SiO_2 used in the first stage), 0.002 ml/min of ethanol feed	microporous MgO/LTA: 23% of ethanol conversion mesoporous MgO/LTA: 45% of ethanol conversion, high production amount of croton aldehyde and high polar C_4 compound
	Zr incorporated microporous and mesoporous BEA zeolites [52]	ethanol-acetaldehyde mixed feed with a molar ratio of 1:1 and 40 ml/min of nitrogen as the carrier gas, 325 °C, atmospheric pressure, 0.5 g of catalyst	microporous Zr-BEA: 55% of conversion and 75% of butadiene selectivity at the initial reaction stage, 35% of conversion and 59% of butadiene selectivity after 6 hours of TOS mesoporous Zr-BEA: 58% of initial conversion, 44% of conversion after 6 hours of TOS, maintained more than 60% of butadiene selectivity at 6 hours of TOS
	1.2%Mg-16%Zr/MFI nanosheet [33]	two-step method in a dual fixed-bed reactor system, *in-situ* generated ethanol-acetaldehyde mixture in the first fixed-bed reactor using 1 g of 20%Cu/SiO_2 as a catalyst and ethanol as a reactant, 1 g of catalyst, T = 350 °C, 1.44 h^{-1} of WHSV, ethanol : acetaldehyde = 2 : 1	conversion: 41.5% of total, 30.1% of ethanol, 64.4% of acetaldehyde product selectivity: 7% of ethylene, 74.6% of 1,3-butadiene, 8.4% of diethyl ether, 5.4% of crotonaldehyde

Table S3. (Continued) Catalytic behaviors of hierarchical zeolites in bioethanol conversion to monomers.

Reaction	Catalyst	Condition	Catalytic performance
Bioethanol to butadiene	Ag-promoted Zr/BEA zeolite [43]	593 K, atmospheric pressure, 2 g of catalyst, molar ratio of EtOH/He = 1, 1.2-3.0 h^{-1} of WHSV	initial formation rate (μmol g^{-1} s^{-1}) parent BEA: 2.5 of ethylene + diethyl ether dealuminated BEA: 1.25 of ethylene + diethyl ether Ag doped dealuminated BEA: 1.20 of ethylene + diethyl ether, 1.89 of acetaldehyde, 0.12 of butadiene Ag-3.5%Zr/BEA: 1.11 of ethylene + diethyl ether, 0.15 of acetaldehyde, 2.99 of butadiene
	bimetallic AgTa/BEA, CuTa/BEA, and ZnTa/BEA zeolite catalysts [34]	598 K, atmospheric pressure, 0.25 g of catalyst, 0.5 h^{-1} of WHSV, time-on-stream = 3.5 h	Ta/BEA: 13.3% of ethanol conversion and 16.4% of butadiene selectivity AgTa/BEA: 82.9% of ethanol conversion and 62.6% of butadiene selectivity CuTa/BEA: 87.9% of ethanol conversion and 72.6% of butadiene selectivity ZnTa/BEA: 51.7% of ethanol conversion and 42.8% of butadiene selectivity
	LiZnHf-MFI nanosheet and microporous catalysts [35]	593 K, atmospheric pressure, 1.0 g of catalyst, 0.47 h^{-1} of WHSV, 3 h of reaction time	LiZnHf-MFI nanosheet: 64.6% of ethanol conversion and 73.0% of butadiene selectivity LiZnHf-MFI microporous: 21.3% of ethanol conversion and 36.4% of butadiene selectivity