Electronic Supplementary Material (ESI) for Green Chemistry.

Conversion of ethanol to 1,3-butadiene over high-performance Mg-ZrOx/MFI nanosheet catalysts via the two-step method

Xianquan Li,[a,b] Jifeng Pang,[a] Chan Wang,[a] Lin Li,[a] XiaoLi Pan,[a]

Mingyuan Zheng,[a, C*] and Tao Zhang[a]

[a] Dalian Institute of Chemical Physics, Chinese Academy of Sciences,

Dalian 116023, P.R. China. E-mail: myzheng@dicp.ac.cn

[b] University of Chinese Academy of Sciences, Beijing 100049, China.

[C] Dalian National Laboratory for Clean Energy, Dalian 116023, People's Republic of China.

Experimental

1.1 Materials

Ethanol (EtOH, 99.7%, Sinopharm), tetraethyl orthosilicate (TEOS, 98%, Aldrich), $Mg(NO_3)_2 \cdot 6H_2O$ (99%, Aldrich), $Cu(NO_3)_2$ (99.5%, Aldrich), $ZrO(NO_3)_2$ (99.9%, Aldrich), tetrapropylammonium hydroxide (TPAOH, 2.0 mol/L in H_2O, Aldrich), and magnesium acetylacetone (99%, Aldrich) were used as received without further purification.

1.2 Catalyst Preparation

Synthesis of 20%Cu/SiO_2: The catalyst was prepared by ammonia evaporation method. In detail, a mixture solution consisting 5 mL ammonium hydroxide, 100 mL deionized water and 0.75 g $Cu(NO_3)_2$ was filled in a flask and stirred for 3 h at 298 K, and then added with 1 g SiO_2 (size <100 mesh, Qingdao Haiyang Chemical Co.). The mixture was heated to 353 K and further stirred until the pH value reached 7. The precipitation was filtered, dried at 373 K overnight, and calcined at 673 K for 4 h. Before used in reaction for ethanol conversion to acetaldehyde, the catalyst was made into tablets, crushed and sieved to 20-40 mesh without reduction.

1.3 Catalytic performance of 20%Cu/SiO_2 for ethanol conversion to acetaldehyde in the first reactor.

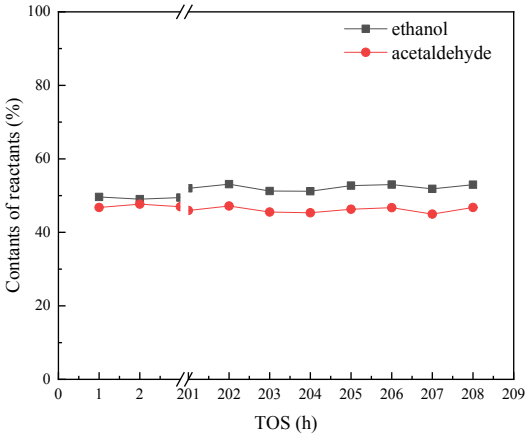

Fig. S1 Contents of ethanol and acetaldehyde in the products of ethanol conversion in the first fixed-bed reactor as a function of reaction time. (The time on stream was started to be counted after the 24 h induction period for catalyst activation)

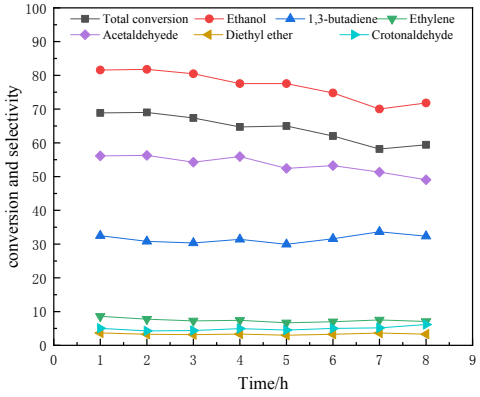

Fig. S2 Catalytic performance of 24Zr/MFI(NS) in ethanol conversion.

Table S1.

Texture property of various MFI(NS) supported Zr catalysts.

Catalyst	S^{a}_{BET} (m^2g^{-1})	S^{b}_{Ext} (m^2g^{-1})	S^{c}_{micro} (m^2g^{-1})	V^{c}_{micro} (cm^3g^{-1})	V^{b}_{meso} (cm^3g^{-1})	Pore[d] (nm)
MFI (NS)	468	268	200	0.1	0.46	3.9
4%Zr/MFI (NS)	445	246	199	0.1	0.44	3.7
16%Zr/MFI (NS)	357	160	197	0.08	0.35	3.6

[a] Total surface area is determined by 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.

Texture property of 16%Zr loaded on different supports.

Catalyst	S^{a}_{BET} (m^2g^{-1})	S^{b}_{Ext} (m^2g^{-1})	S^{c}_{micro} (m^2g^{-1})	V^{c}_{micro} (cm^3g^{-1})	V^{b}_{meso} (cm^3g^{-1})	Pore[d] (nm)
16%Zr/MFI(NS)	357	160	197	0.08	0.35	3.6
16%Zr/MFI(micro)	336	80	256	0.21	0.1	0.8
16%Zr/SiO_2	393	366	27	0.01	0.62	6.2

[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 S3.

Texture property of various Mg-Zr/MFI(NS) catalysts.

Catalyst	S^{a}_{BET} (m^2g^{-1})	S^{b}_{Ext} (m^2g^{-1})	S^{c}_{micro} (m^2g^{-1})	V^{c}_{micro} (cm^3g^{-1})	V^{b}_{meso} (cm^3g^{-1})	Pore[d] (nm)
1.2Mg-16%Zr/MFI(NS)	354	178	176	0.09	0.36	3.8
1.2%Mg-16%Zr/MFI(NS) organic Mg	360	180	180	0.09	0.37	3.7
19.2%Mg-16%Zr/MFI(NS)	228	71	157	0.07	0.25	4.2
1.2%Mg/MFI(NS)	446	240	206	0.1	0.43	3.8
19.2%Mg/MFI(NS)	419	194	225	0.11	0.4	4.1

[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.

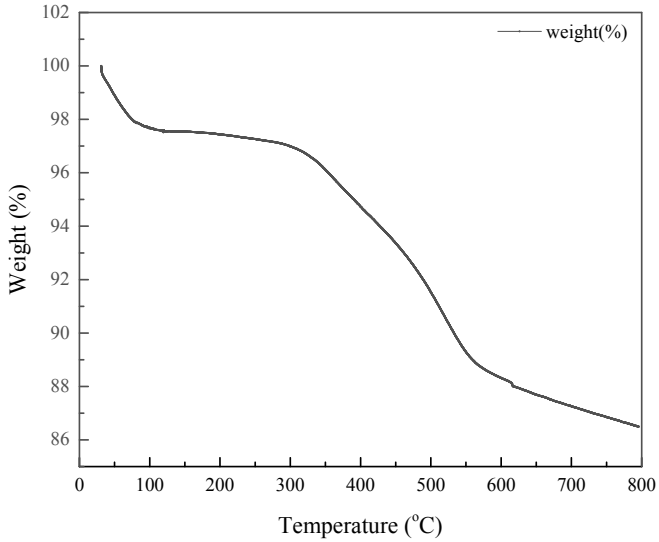

Fig. S3 TG curve of 1.2%Mg-16%Zr/MFI(NS) catalyst after 7 days reaction.

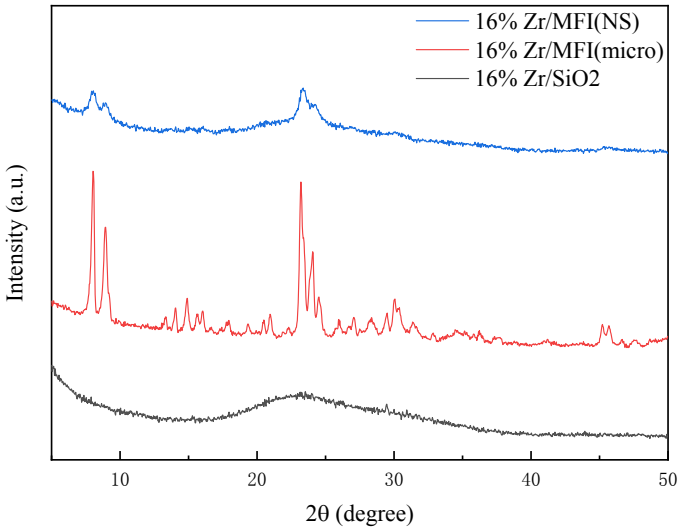

Fig S4. XRD patterns of Zr catalysts loaded on different supports.

Fig. S5 TEM image (a), HAADF-STEM image (b) and EDS mapping (c-g) of 1.2%Mg-16%Zr/MFI(NS).

Fig. S6 SEM images of the fresh (left image) and the spent (right image) 1.2%Mg-16%Zr/MFI(NS).

Fig. S7 HAADF-STEM image (a) and EDS mapping (b-f) of the spent 1.2%Mg-16%Zr/MFI(NS).

Fig. S8 XRD patterns of the spent 1.2%Mg-16%Zr/MFI(NS).