

Supporting Information

Bayberry-like ZnO/MFI Zeolite as High Performance Methanol- to-aromatics Catalyst

Ning Wang, Weizhong Qian,* Kui Shen, Chang Su, and Fei Wei

*Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of
Chemical Engineering, Tsinghua University, Beijing 100084, PR China*

E-mail: qianwz@tsinghua.edu.cn

EXPERIMENTAL SECTION

Synthesis Procedures

Preparation of bayberry-like MFI zeolite: The silicalite-1 nanocrystals were firstly synthesized by a method similar to that previously.¹ 24.3 g TEOS, used as silica source, was added into 25.8 g TPAOH (25 wt % in water) with continuous stirring. The molar composition of the gel was 92SiO₂: 25TPAOH: 479H₂O: 368EtOH. The gel was homogenized at 25 °C for 6 h and then was hydrothermally treated at 90 °C for 72 h, washed and centrifuged. In the second step, a solution of NaAlO₂ (0.11 g; 46.78% Al₂O₃, 28.43% Na₂O) in distilled water (1 g) was added with 0.04 g nanocrystalline silicalite-1. Then 2 g round MS microspheres with uniform size of ~15 μm (Knowledge & Benefit Sphere Tech. Co.; LTD.) were impregnated using the above aluminum-contained seeding solution. The obtained impregnated MS spheres were then dried at 90°C. In the third step, 2 g seeded MS spheres were placed in a raised PTFE holder which was placed horizontally in the middle of a PTFE lined stainless steel autoclave (80 mL). 5 mL of distilled water was poured at the bottom of the autoclave, which was then enclosed and heated in an oven to carry out a steam-assisted crystallization (SAC) process at 180°C for 1 day. After cooling to room temperature, the products were dried at 110°C overnight and subsequently calcinated in air at 550 °C for 6 h to remove the template.

Preparation of bayberry-like ZnO/MFI zeolite: The bayberry-like ZnO/MFI zeolite was synthesized using the similar route except that MS spheres were impregnated with 2 mL of 0.46 M Zn(NO₃)₂·6H₂O aqueous solution in the first step.

Characterization

X-ray diffractions (XRD) were recorded on a Rigaku D/Max-RB diffractometer with Cu K α Radiation at 40 kV and 120 mA. Scanning electron microscope (SEM) images were obtained by a high-resolution scanning electron microscope (JEOL, JSM-7401) at 3.0 kV. Energy-dispersive X-ray (EDX)

analysis was performed using a JSM-7401F apparatus at 15.0 kV with the analytical software INCA. TEM experiments were performed on a high-resolution transmission electron microscope (JEOL, JEM-2010, exited at 120kV) equipped with selected area electron diffraction (SAED). Ar physisorption was performed on an Autosorb-IQ2-MP-C system (Quantachrome) at $-186\text{ }^{\circ}\text{C}$. The pore size distribution was evaluated by an NLDFIT method using the silica cylindrical pore, adsorption branch model. ^{27}Al and ^{29}Si MAS NMR experiments were performed on Bruker AVANCE III 600 spectrometer at a resonance frequency of 156.4 MHz and 119.2 MHz, respectively. ^{27}Al MAS NMR spectra were recorded on a 4 mm probe by small-flip angle technique with a pulse length of $0.5\text{ }\mu\text{s}$ ($<\pi/12$) and a 1s recycle delay. ^{29}Si MAS NMR spectra with high-power proton decoupling were recorded on a 4 mm probe with a spinning rate of 12 kHz, a $\pi/4$ pulse length of $2.6\text{ }\mu\text{s}$, and a recycle delay of 80 s. The chemical shifts of ^{29}Si and ^{27}Al were referenced to TMS and 1 mol/L aqueous $\text{Al}(\text{NO}_3)_3$, respectively.

Catalytic performance testing

For MTA reactions, calcined MFI zeolites were all brought into H-form by ion exchange in 1 M NH_4NO_3 and subsequent calcination at $550\text{ }^{\circ}\text{C}$. The MTA reaction were performed at the conditions of 1 atm, $475\text{ }^{\circ}\text{C}$ and $\text{WHSV}=0.75\text{ h}^{-1}$ (under N_2 flow ($10\text{ mL}\cdot\text{min}^{-1}$) in a conventional fixed bed stainless steel reactor (13.0 mm i.d) equipped with a thermocouple in the middle of the catalyst bed. 0.5 g of catalyst was placed in the fixed bed reactor. The flow rate of pure methanol and N_2 was controlled using a dual micro-plunger pump and the mass flow controllers, respectively. The products (hydrocarbons) were analyzed using two flame ionization detector (FID). The conversion of methanol and the selectivity of different products were calculated (carbon base) by considering oxygenates (methanol and dimethylether) as unconverted species.

Table S1 Textural parameters of bayberry-like MFI zeolite, ZSM-5 NPs and microsized ZSM-5.

Type	Theoretical Si/Al atomic ratio	Si/Al atomic ratio ^a	S _{BET} (m ² /g)	V _t ^b (cm ³ /g)	V _{mic} ^b (cm ³ /g)	V _{meso} (cm ³ /g)
Bayberry-like MFI zeolite	8	8.1	442.7	0.299	0.147	0.152
	12	10.5	455.2	0.296	0.153	0.143
	25	23.1	453.3	0.260	0.112	0.148
ZSM-5 NPs	25	25.5	484.0	0.685	0.116	0.569
Microsized ZSM-5	25	28.0	423.6	0.257	0.166	0.091

^a Si/Al atomic ratios measured by ICP-AES.

^b Pore volume determined via the NLDFT method.

Quantitatively, the pore volume of micropores and mesopores was in the range of 0.112–0.153 mL/g and 0.143–0.152 mL/g, respectively. In comparison, the pore volume of micropores and mesopores of microsized ZSM-5 was 0.166 mL/g and 0.091 mL/g, respectively. And the pore volume of micropores and mesopores of a typically ZSM-5 NPs was 0.116 mL/g and 0.569 mL/g, respectively. These pore differences would exhibit different mass transfer capability.

Table S2 Textural properties of the bayberry-like MFI zeolite crystallized at various times.

Crystallization time (min)	S _{BET} (m ² /g)	V _t ^a (cm ³ /g)	V _{mic} ^a (cm ³ /g)	V _{meso} (cm ³ /g)
0	48.1	0.260	0.000	0.260
2	40.5	0.151	0.000	0.151
5	91.0	0.228	0.025	0.203
10	201.1	0.252	0.034	0.218
14	307.6	0.177	0.083	0.094
18	380.3	0.205	0.122	0.083

^a Pore volume determined via the NLDFIT method.

Table S3 Product selectivity of MTA reaction over Zn/La/ZSM-5 catalyst.^{2,3}

Si/Al molar ratio	Selectivity of hydrocarbons									
	CH ₄	C ₂	C ₃	C ₄	C ₅	C ₆	C ₆ H ₆	C ₇ H ₈	C ₈ H ₁₀	C ₉ H ₁₂
19	2.5	3.1	21.2	8.2	4.8	3.8	6.1	23.2	22.3	4.6
25	2.5	3.2	14.9	8.4	1.7	4.9	4.7	22.9	29.0	7.3
30	2.0	3.8	17.2	9.8	2.4	6.7	4.4	21.6	25.9	5.9
50	2.0	4.2	14.1	12.5	3.9	8.6	3.6	19.7	24.8	6.2

437°C, 0.1MPa, WHSV=0.8 h⁻¹, the conversion of methanol is 100%, data were obtained at 4h on stream.

Table S4 Product selectivity of MTA reaction over conventional Zn/ZSM-5 catalyst.⁴

Si/Al molar ratio	Conversion of methanol (%)	Selectivity (%)						Total aromatics (%)
		C ₁ -C ₅ alkanes	C ₂ -C ₅ olefins	C ₆ ben.	C ₇ ben.	C ₈ ben.	C ₉₊ ben.	
30	99.03	20.83	28.95	1.76	11.19	36.09	1.16	50.22
60	96.80	16.77	31.23	0.64	5.29	34.57	11.49	51.99
90	95.54	16.02	27.43	0.81	7.19	31.88	16.65	56.54

Table S5 Methanol conversion and product selectivity over bayberry-like MFI zeolite, microsized ZSM-5 and ZSM-5 NPs in MTA reaction.

Si/Al molar ratio	Conversion of methanol (%)	Selectivity (%)						Total aromatics (%)
		C ₁ -C ₅ alkanes	C ₂ -C ₅ olefins	C ₆ ben.	C ₇ ben.	C ₈ ben.	C ₉₊ ben.	
Bayberry-like ZSM-5	97.62	9.80	18.18	2.34	10.65	49.37	9.66	72.02
ZSM-5 NPs	97.57	15.88	22.46	0.46	4.53	25.09	31.58	61.66
Microsized ZSM-5	95.32	23.59	34.24	0.89	7.07	35.65	22.15	65.76

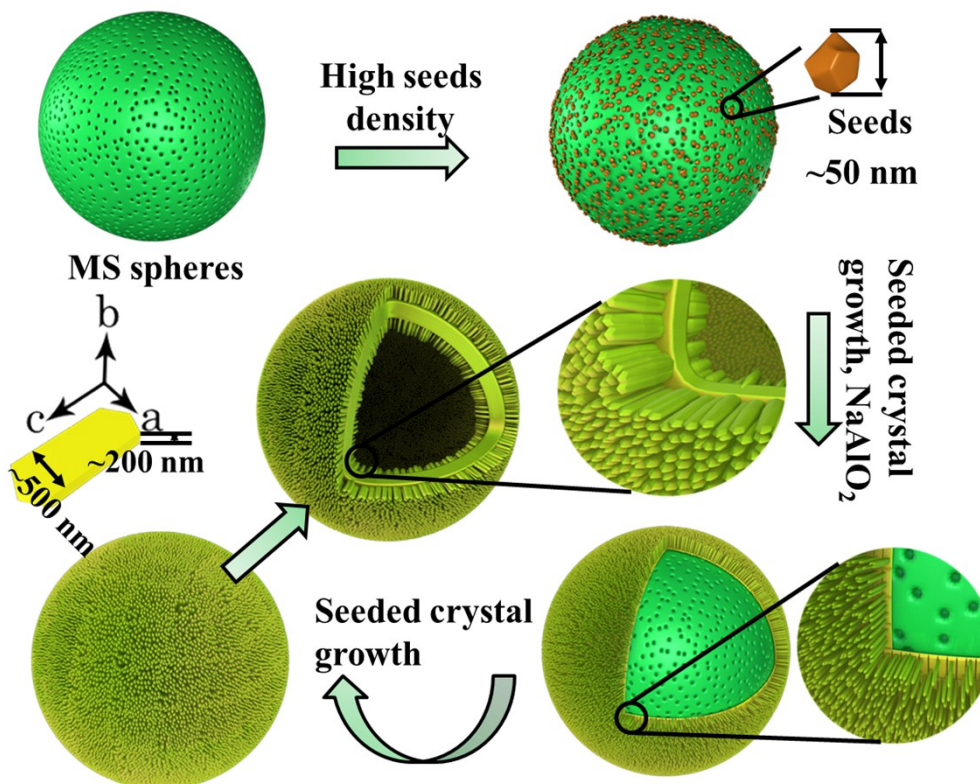


Fig. S1 Schematic of the synthetic procedure for bayberry-like MFI zeolite structure by a quasi-solid-state crystallization process.

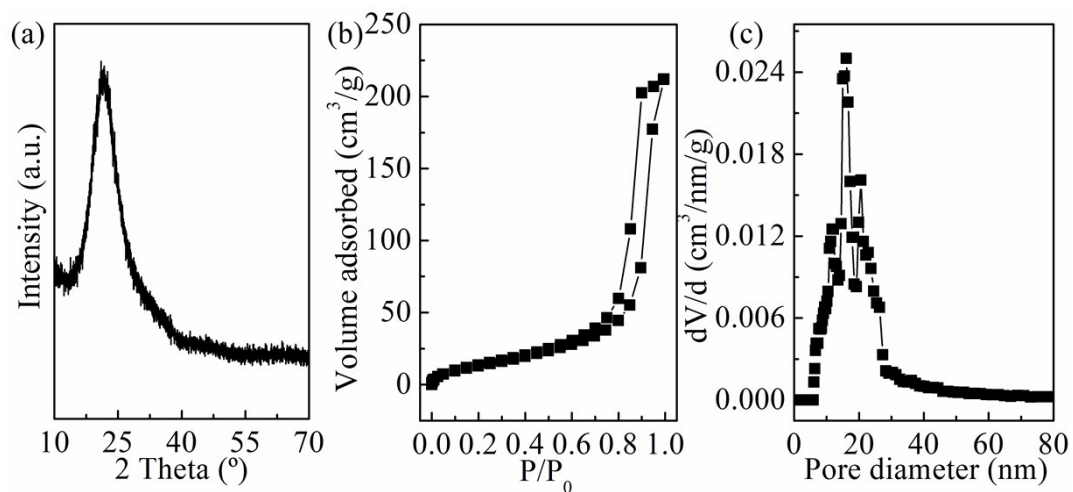


Fig. S2 (a) XRD patterns, (b) Ar physisorption isotherms, and (c) Pore size distribution of MS spheres.

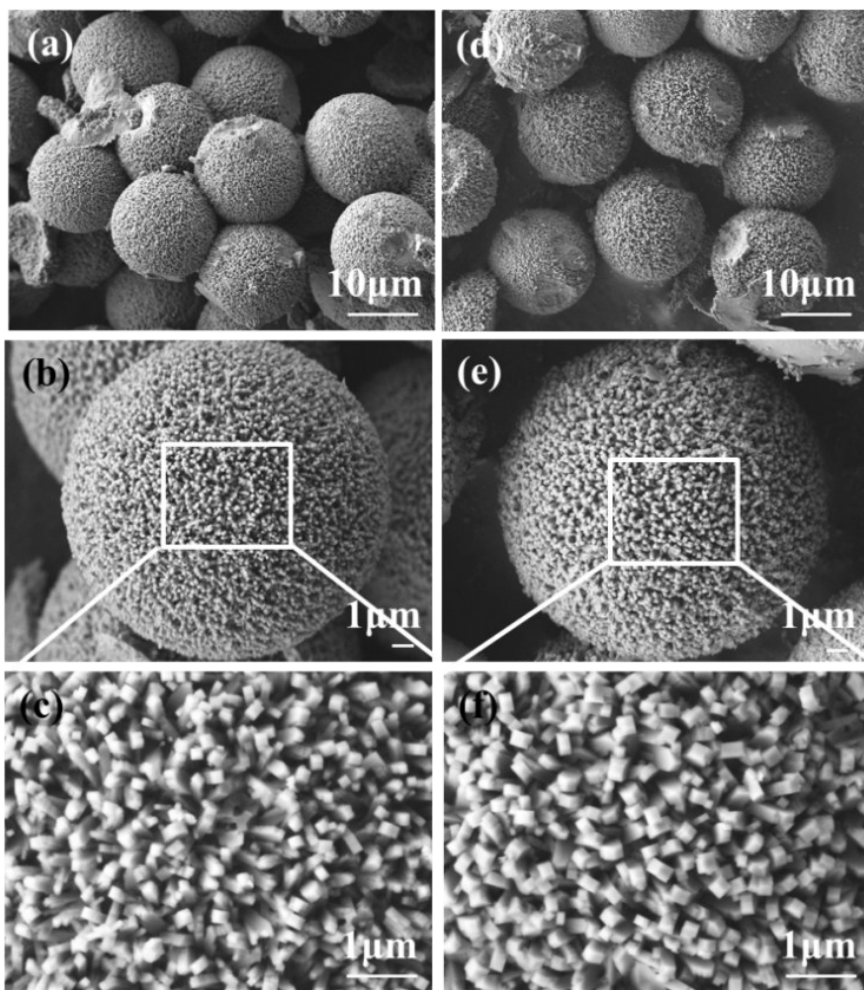


Fig. S3 SEM images of bayberry-like MFI zeolite with a Si/Al ratio of (a-c) 12, (d-f) 25.

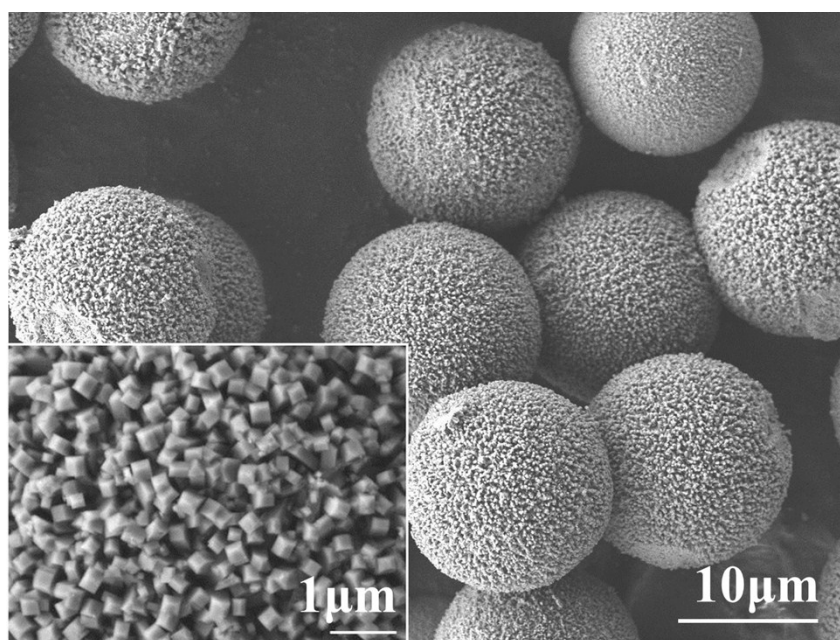


Fig. S4 SEM images of bayberry-like MFI zeolite after calcination (in air, 1000 °C, 2h) and sonication (high frequency (HF) = 50kHz, 100 W, 1h).

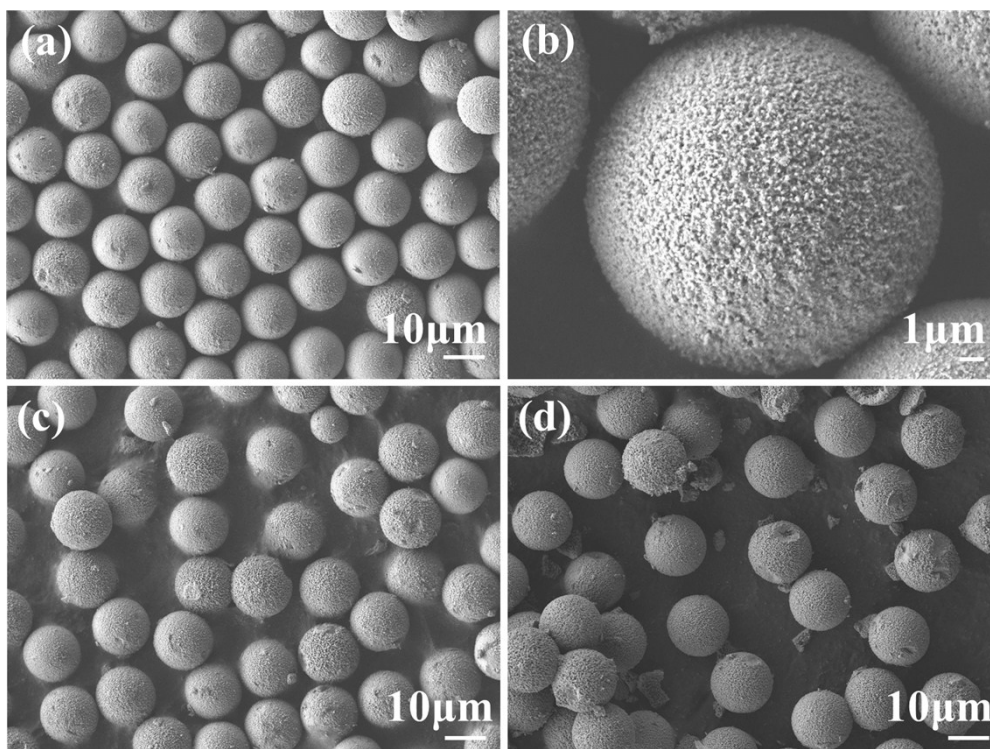


Fig. S5 SEM images of sample crystallized at (a and b) 2h, (c) 5h, (d) 10h.

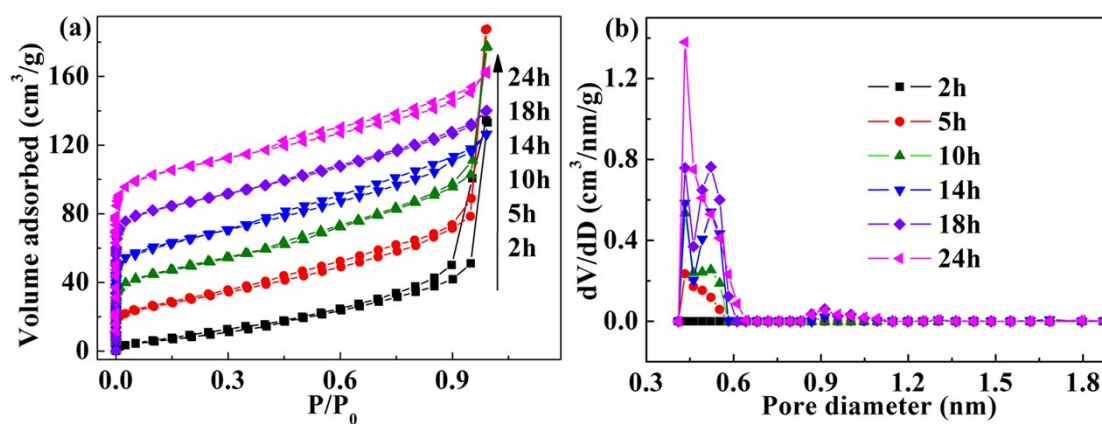


Fig. S6 (a) Ar physisorption isotherms and (b) corresponding NLDFT micropore size distributions of sample at different crystallization times.

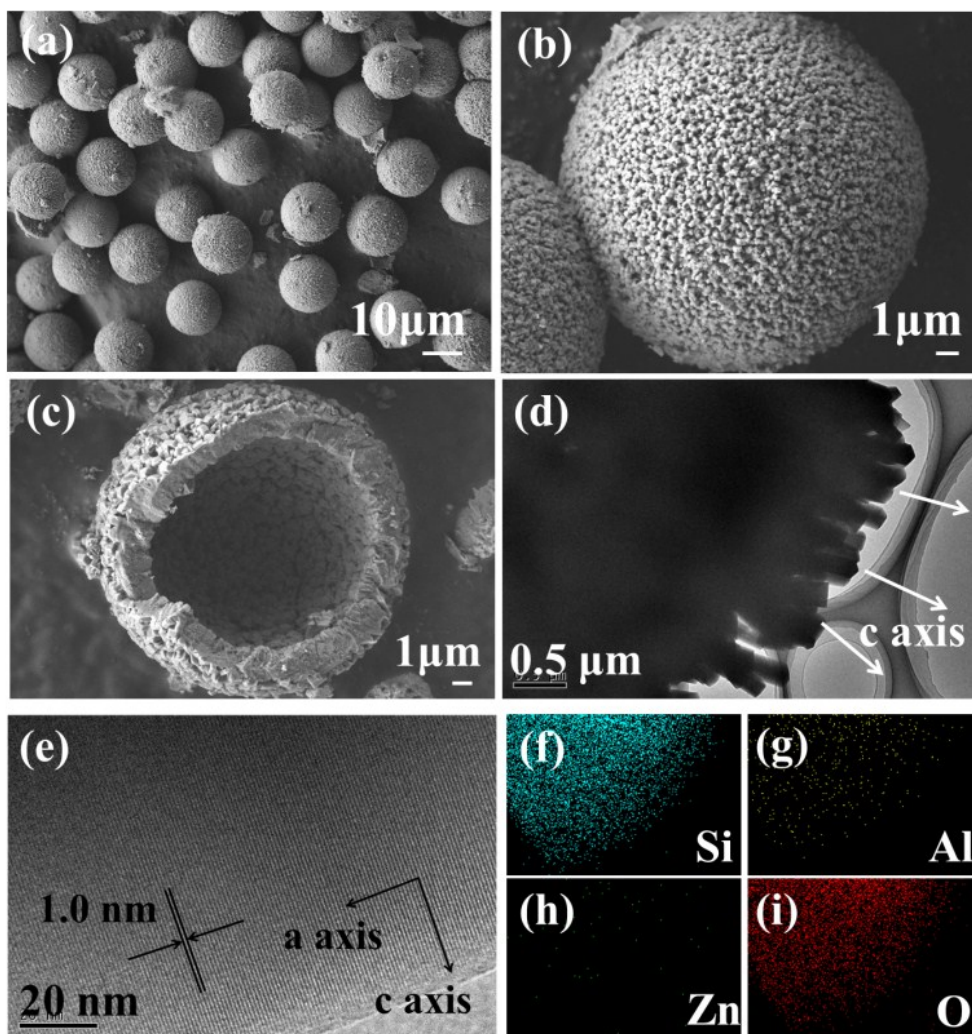


Fig. S7 In-situ obtained bayberry-like ZnO/MFI zeolite. (a-c) SEM images; (d and e) TEM images; (f-i) EDX element mapping.

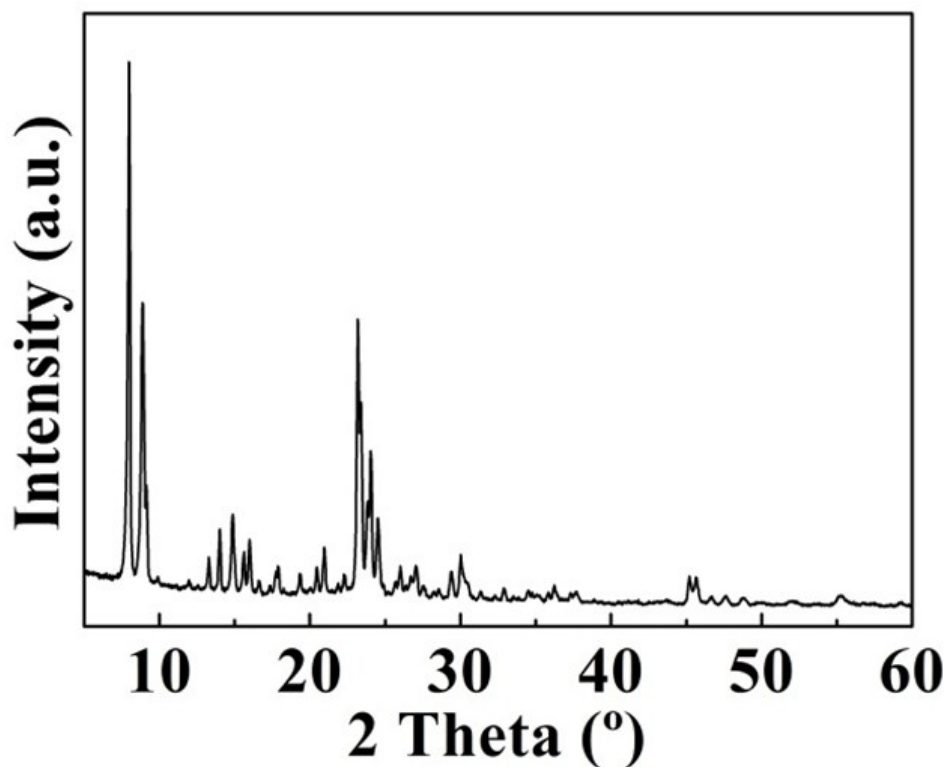


Fig. S8 XRD patterns of In-situ obtained bayberry-like ZnO/MFI zeolite.

References

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