

Supporting Information

Anion-promoted increase of the SiO₂/Al₂O₃ ratio of zeolites

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1. Experimental Section

1.1 Chemicals and materials

The chemicals were LUDOX HS-40 colloidal silica (Sigma-Aldrich), LUDOX AS-40 colloidal silica (Sigma-Aldrich), sodium chloride (NaCl, 99.5%, Tianjin Fuchen Chemical Reagents Company), sodium iodide (NaI, 99%, Tianjin Fuchen Chemical Reagents Company), sodium hydroxide (NaOH, Beijing Chemical Works), sodium aluminate (53% Al₂O₃, 41% Na₂O and 6% H₂O, Sigma-Aldrich Co), aluminium hydroxide (Sigma-Aldrich Co) and deionized water (18.2 MΩ*cm). Seeds were commercial (**MOR**: Nankai University Catalyst Co., Ltd. SiO₂/Al₂O₃ = 25; ZSM-5: Luoyang Jalon Micro-nano New Materials Co., Ltd. SiO₂/Al₂O₃ = 30). All chemicals were used without further purification.

1.2 Characterization

The X-ray diffraction patterns (XRD) were obtained by a Rigaku D/max-2550 diffractometer (Rigaku Corporation, Tokyo, Japan) with Cu Kα radiation ($\lambda = 1.5418$ Å). The crystal size and morphology were measured by scanning electron microscopy (SEM) via a JSM-7800F (JEOL) electron microscope (JEOL Ltd., Tokyo, Japan). Solid-state ²⁹Si MAS NMR and ²⁷Al MAS NMR experiments were performed on a Bruker Avance Neo 600Mz WB spectrometer with BBO MAS probe operating at a magnetic field strength of 14.1 T (Bruker Company, Karlsruhe, Germany). Chemical composition was determined with inductively coupled plasma (ICP) analyses carried out on a thermo Fisher Scientific iCAP7600 DUO (Thermo Fisher Scientific, Waltham, WM). Elemental mapping images were taken on an energy dispersive spectrometer (EDS) (Oxford Instruments, High Wycombe, UK). The temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. The samples were dissolved in HNO₃/HCl/HF aqueous solution before measurement.¹

1.3 Synthesis of samples

Synthesis of MOR with various amount of NaI

Took 6 beakers (25 mL) and labelled each sequentially. The following steps were applied to the 6 beakers otherwise mentioned. Typically, 0.236 g of NaOH was added to 2.364 g of deionized water under stirring. Subsequently, 0.107 g of sodium alumina

was added and kept stirring for 10 minutes. Then, 5.4 g of deionized water was added and the mixture was stirred for additional 10 minutes. Subsequently, 2.5 g of silica sol (LUDOX HS-40) was added. The slurry was strongly stirred at ambient temperature for 30 minutes. After that, 6 beakers each was added with 0, 0.2, 0.3, 0.4, 0.5 or 0.6 g of NaI sequentially and the slurry were kept stirring for 20 minutes. Finally, 0.08 g of seed of **MOR** was added to each beaker. After stirring for 10 minutes, each mixture was transferred into a Teflon-lined stainless-steel autoclave. The crystallization was conducted in an oven at 170 °C for 24 hours. The products were separated by centrifugation with 10000 rpm and the repeated re-dispersion/centrifuging (3 times) in deionized water was performed in order to wash the solid products. Finally, the solid products were dried in oven at 60 °C overnight.

Synthesis of MOR with NaCl

The amounts of NaOH, sodium aluminate, LUDOX HS-40, **MOR** seeds and, deionized water as well as the procedure of the preparation of the reaction mixture, was the same as above. NaI was replaced by 0.155 g of NaCl. The products were separated by centrifugation with 10000 rpm and the repeated re-dispersion/centrifuging (3 times) in deionized water was performed in order to wash the solid products. Finally, the solid products were dried in oven at 60 °C overnight.

Synthesis of MOR in the absence/presence of NaI with various crystallization time

Took 14 beakers (25 mL) and labelled each sequentially. The amounts of NaOH, sodium aluminate, LUDOX HS-40, **MOR** seeds and, deionized water as well as the procedure of the preparation of the reaction mixture, was the same as above. 0.4 g of NaI was added sequentially to the 7 beakers. The crystallization was conducted in an oven at 170 °C for 0, 2, 4, 6, 8, 10 and 24 hours. The products were separated by centrifugation with 10000 rpm and the repeated re-dispersion/centrifuging (3 times) in deionized water was performed in order to wash the solid products. Finally, the solid products were dried in oven at 60 °C overnight.

Synthesis of NaY zeolite in the absence/presence of NaI

Took 2 beakers (25 mL) and labelled each sequentially. The following steps were applied to the 2 beakers otherwise mentioned. Typically, 0.762 g of sodium alumina and 0.514 g of NaOH were added to 5.481 g of deionized water under stirring. Subsequently, 5.625 g of colloidal silica (LUDOX AS-40) was added and kept stirring for 4 hours. Then, 0.286 g of NaI was added to one of beaker. After stirring for 10

minutes, each mixture was transferred into a Teflon-lined stainless-steel autoclave. The molar composition of the initial mixture is 9.5 SiO₂: 1 Al₂O₃: 2.9 Na₂O: 124.9 H₂O. The crystallization was conducted in an oven at 100 °C for 72 hours. The products were separated by centrifugation with 10000 rpm and the repeated re-dispersion/centrifuging (3 times) in deionized water was performed in order to wash the solid products. Finally, the solid products were dried in oven at 60 °C overnight.

Synthesis of ZSM-5 zeolite in the absence/presence of NaI

Took 2 beakers (25 mL) and labelled each sequentially. The following steps were applied to the 2 beakers otherwise mentioned. Typically, 0.192 g of NaOH was added to 9.76 g of deionized water under stirring. Subsequently, 0.143 g of aluminum hydroxide was added and kept stirring for 20 minutes. Then, 3 g of colloidal silica (LUDOX HS-40) was then added and the mixture was stirred for additional 2 hours. After that, 0.103 g of NaI was added to one of beaker. The mixtures were kept stirring for 10 minutes. Finally, 0.06 g of seed of ZSM-5 was added to the 2 beakers. After stirring for 10 minutes, each mixture was transferred into a Teflon-lined stainless-steel autoclave. The molar composition of the initial mixture is 27.1 SiO₂: 1 Al₂O₃: 4.8 Na₂O: 829.5 H₂O. The crystallization was conducted in an oven at 180 °C for 24 hours. The products were separated by centrifugation with 10000 rpm and the repeated re-dispersion/centrifuging (3 times) in deionized water was performed in order to wash the solid products. Finally, the solid products were dried in oven at 60 °C overnight.

1.4 Computational details

The density functional theory calculations were performed by Gaussian 09 program.² B3LYP functional³⁻⁴ with the Grimme's DFT-D3 dispersion correction⁵ was used. 6-311+G(d,p) basis set was used to describe C, H, O, Si, Na and Al and def2-TZVP basis set was used for I atom. The SMD solvent model⁶ was employed to reappear the solvent effect of water. All reactants and products were confirmed to be the local minima without imaginary frequency, and the transition states were also confirmed by frequency calculation and intrinsic reaction coordinate.

2. Supplementary Figures and Tables

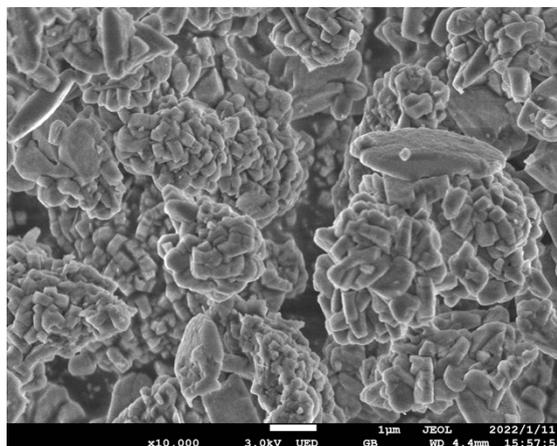


Fig. S1 SEM image of MOR seeds. Scale bar = 1 μm.

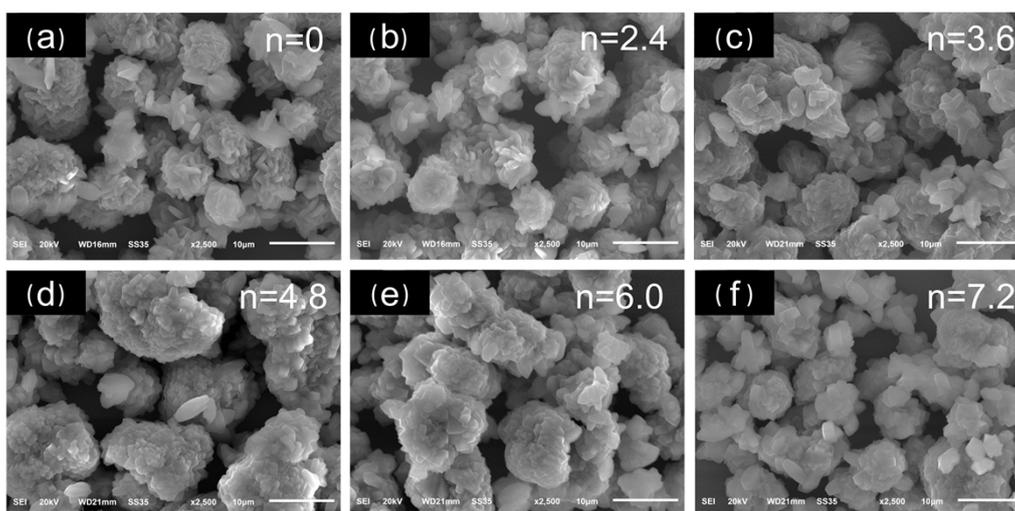


Fig. S2 SEM images of the products crystallized from the initial mixture with a molar composition of 29.6 SiO₂: 1 Al₂O₃: 6.1 Na₂O: 852.6 H₂O: n NaI ((a) n = 0, (b) n = 2.4, (c) n = 3.6, (d) n = 4.8, (e) n = 6.0, (f) n = 7.2). Scale bar = 10 μm.

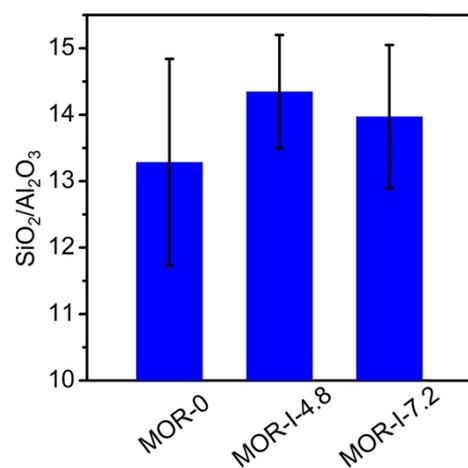


Fig. S3 SiO₂/Al₂O₃ ratio of **MOR-0**, **MOR-I-4.8** and **MOR-I-7.2** measured by ICP with error bars. (The average value of SiO₂/Al₂O₃ ratio for **MOR-0**, **MOR-I-4.8** and **MOR-I-7.2** is 13.28, 14.34 and 13.97, respectively).

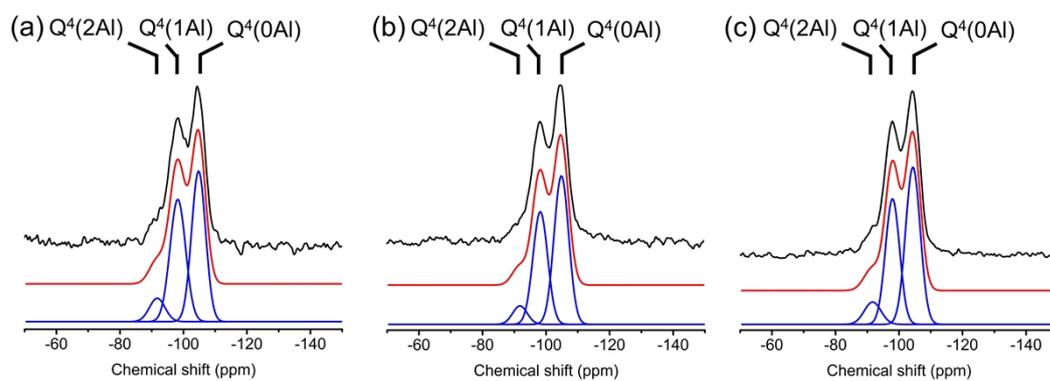


Fig. S4 The solid ²⁹Si MAS NMR spectra of **MOR-0** (a), **MOR-I-4.8** (b) and **MOR-I-7.2** (c).

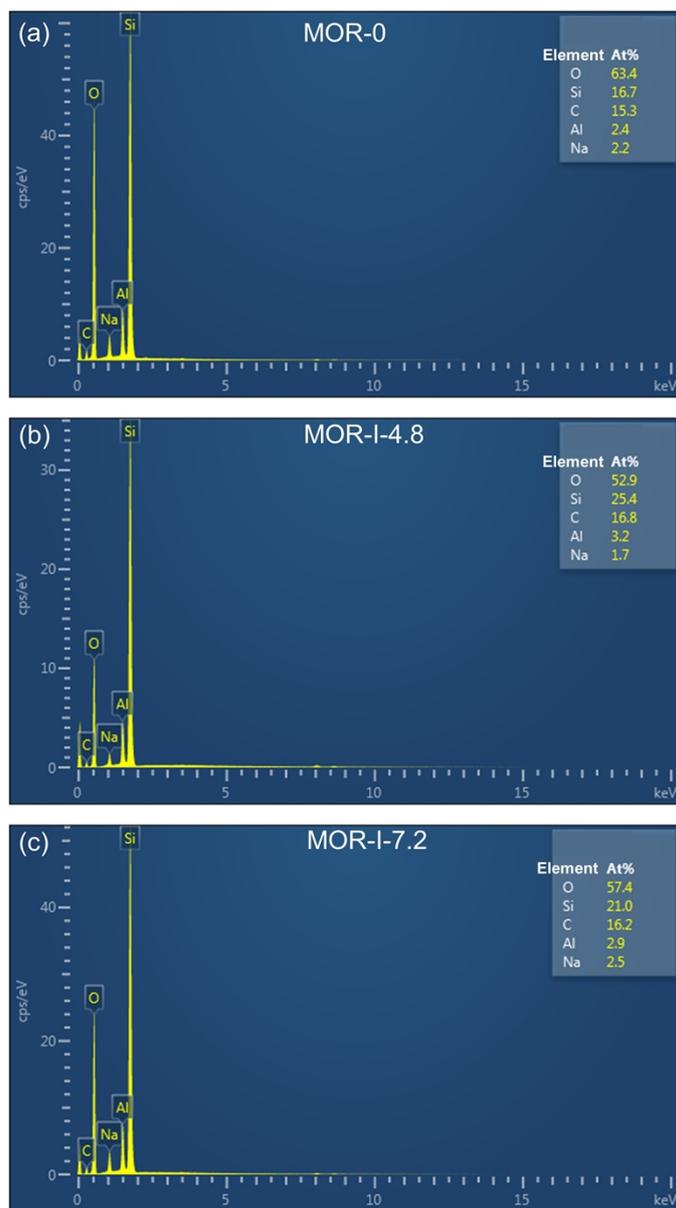


Fig. S5 Elemental analysis data of EDS for Si and Al of (a) **MOR-0**, (b) **MOR-I-4.8** and (c) **MOR-I-7.2**.

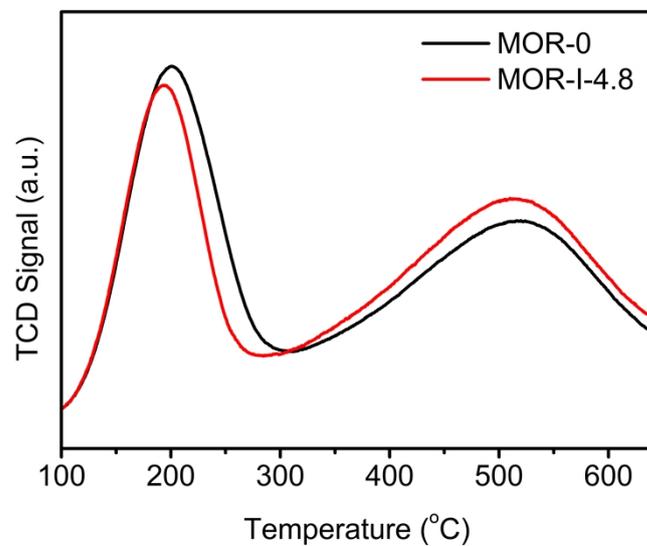


Fig. S6 NH₃-TPD curves of H-MOR-0 and H-MOR-I-4.8.

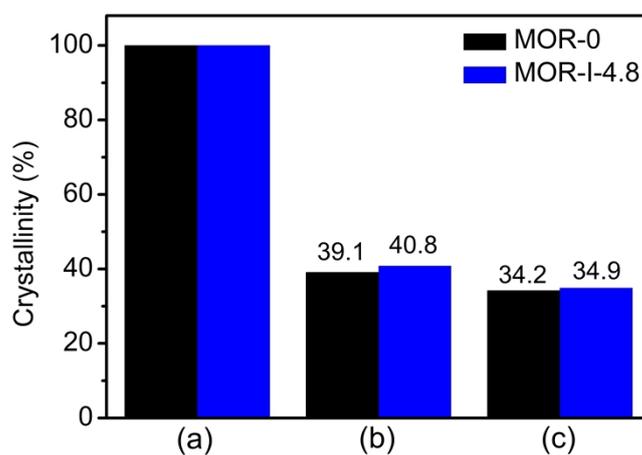


Fig. S7 Relative crystallinity of as-synthesized samples (a) and samples treated at 700 °C in 10% steam for 1 h (b) and calcined at 800 °C for 1 h (c).

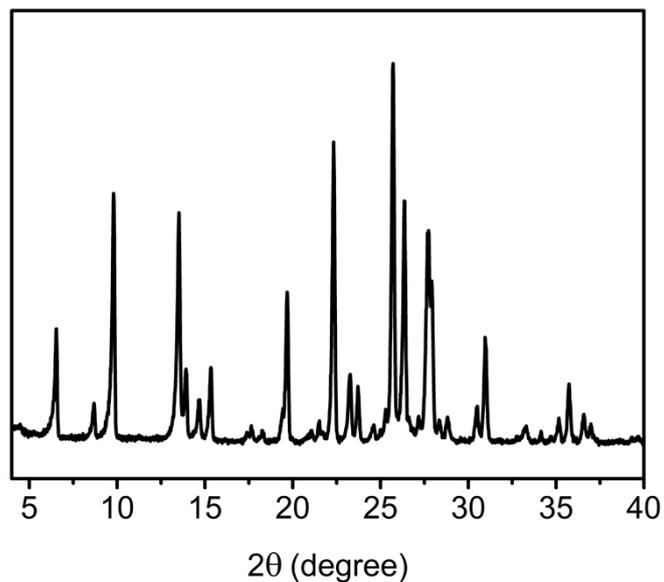


Fig. S8 XRD pattern of **MOR** crystallized from the initial mixture in the presence of NaCl.

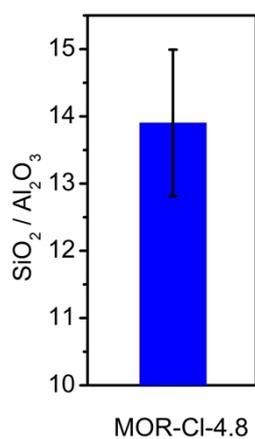


Fig. S9 SAR of **MOR-CI-4.8** measured by ICP with error bar. (The average value of $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of **MOR-CI-4.8** is 13.90)

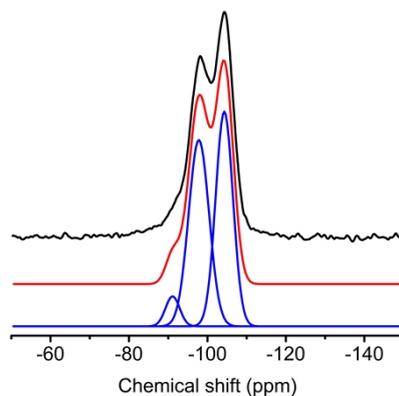


Fig. S10 Solid ^{29}Si MAS NMR spectra of **MOR-CI-4.8**. (The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of **MOR-CI-4.8** measured by solid-state ^{29}Si NMR is 13.65)

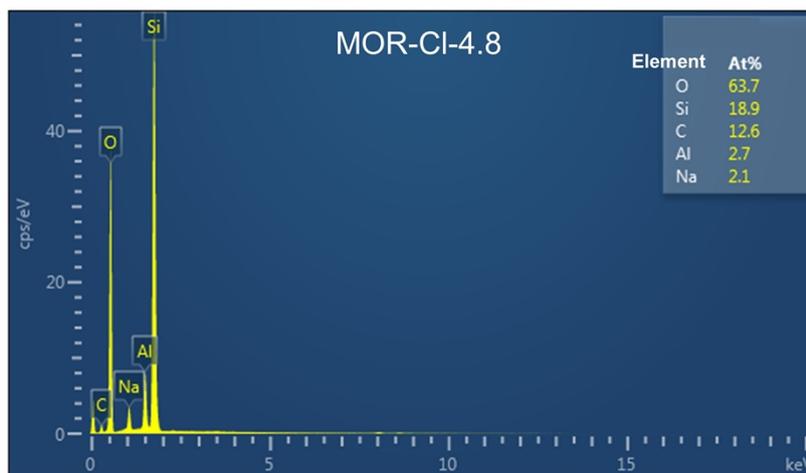


Fig. S11 Elemental analysis data of EDS for Si and Al of **MOR-CI-4.8**. (The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of **MOR-CI-4.8** is 14.)

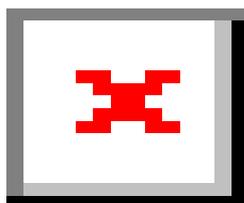


Fig. S12 SEM image of **MOR** crystallized from the initial mixture in the presence of NaCl.

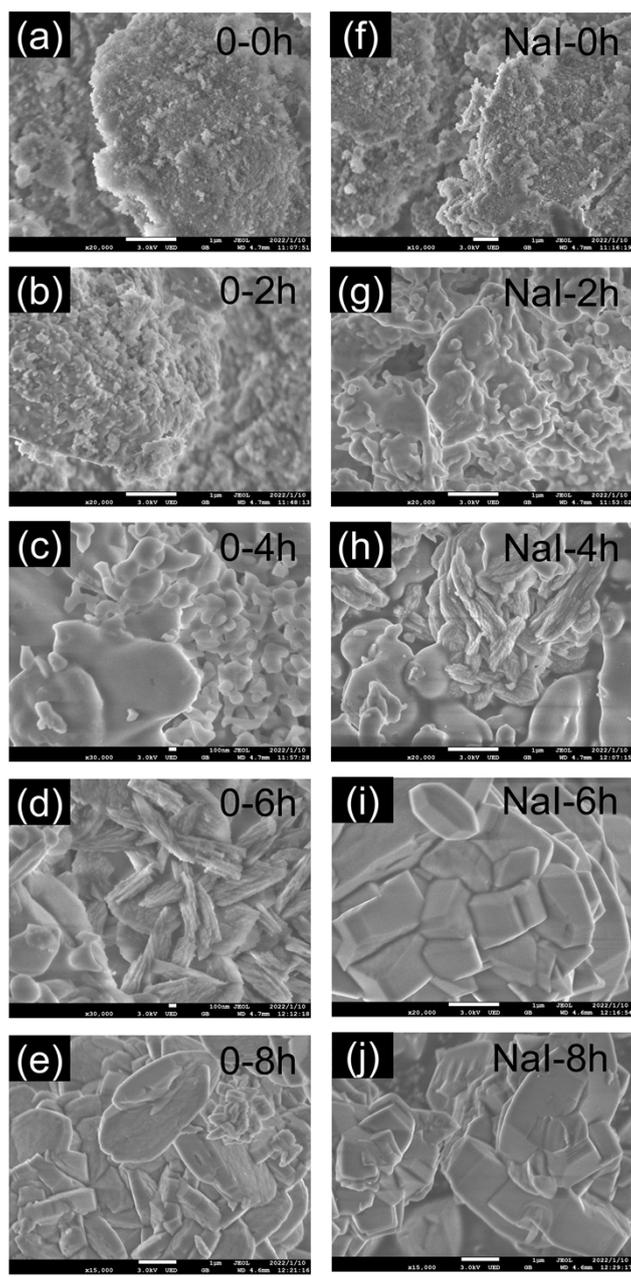


Fig. S13 SEM images of MOR crystallized from the initial mixture in the absence (a-e)/presence (f-j) of NaI at the crystallization time of 0, 2, 4, 6 and 8 h. Scale bar = 1 μ m (a, b, e-j), scale bar = 100 nm (c, d).

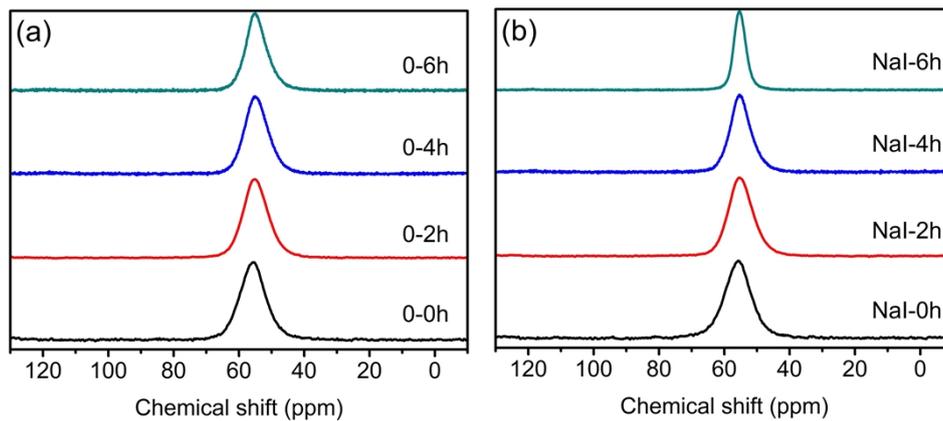


Fig. S14 ^{27}Al MAS NMR spectra of the products crystallized from the initial mixture in the absence (a)/presence (b) of NaI at the crystallization time of 0, 2, 4 and 6 h.

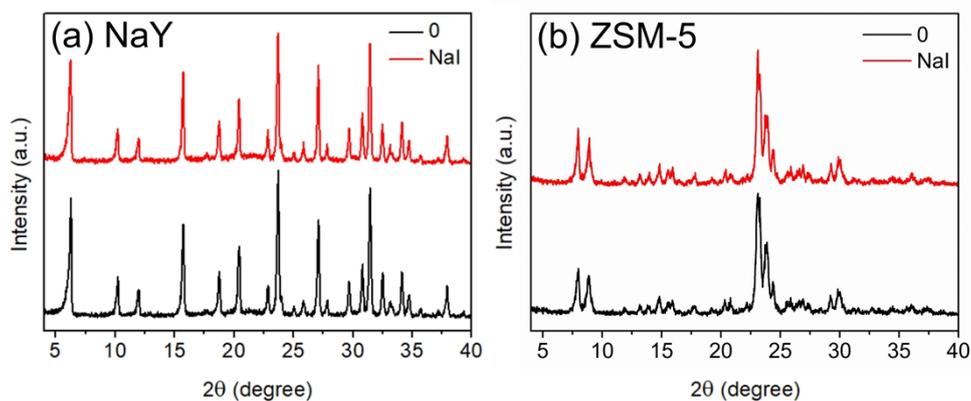


Fig. S15 XRD patterns of NaY (a) and ZSM-5 (b) crystallized from the initial mixtures in the absence/presence of NaI.

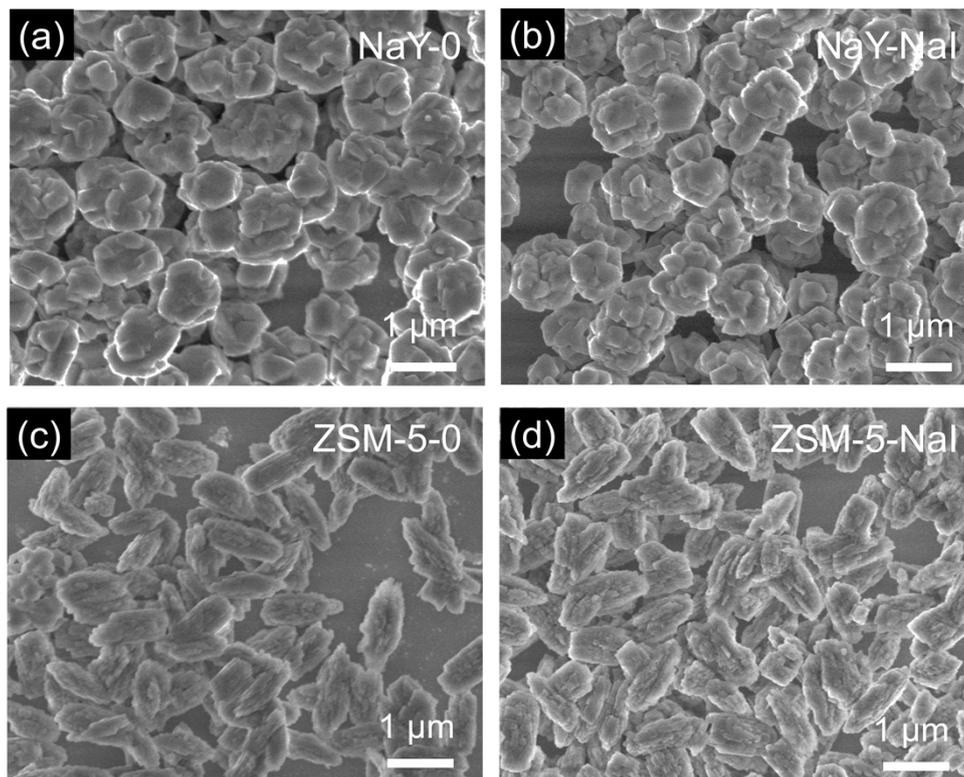


Fig. S16 SEM images of zeolite NaY (a, b) and ZSM-5 (c, d) crystallized from the initial mixture in the absence (a, c)/presence (b, d) of NaI.

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