

Supporting Information

Synthetic and Natural MOR Zeolites as High-Capacity Adsorbents for the Removal of Nitrous Oxide

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Experimental Section

Preparation of zeolites: The following zeolites were purchased: MOR (HSZ-642NAA, Si/Al ratio = 9, Tosoh), MOR (HSZ-660NAA, Si/Al ratio = 15, Tosoh), MFI (HSZ-822HOA, Si/Al ratio = 12, Tosoh), FAU (HSZ-320NAA, Tosoh), 13X (Si/Al ratio = 1.25, FUJIFILM Wako Pure Chemical Corporation), 4A (Si/Al ratio = 1, FUJIFILM Wako Pure Chemical Corporation), silica gel (Fuji Silysia Chemical, Ltd) and activated carbon (FUJIFILM Wako Pure Chemical Corporation). The MOR zeolite with a Si/Al ratio of 5.5 was synthesized according to the previous study.¹ To be brief, the synthesis of this MOR zeolite involved the following chemicals as starting materials: Cab–O–Sil (fumed silica, grade M5, Cabot), sodium aluminate (Wako) and sodium hydroxide (50 wt% in water, Wako). Sodium hydroxide solution was firstly diluted with distilled water, followed by the addition of sodium aluminate. After obtaining a transparent solution, Cab–O–Sil was added and then vigorously mixed to obtain a synthesis mixture with a composition of 0.275 Na₂O: 0.025 Al₂O₃: 1 SiO₂: 25 H₂O. This mixture was transferred to an autoclave (Parr, #4749) and subject to the hydrothermal treatment at 140 °C for 3 d under rotation (40 rpm).

Ion-exchange of zeolites: Aqueous ion-exchanges were performed over the commercial MOR zeolite with a Si/Al ratio of 9 with different nitrate or chloride salts in order to study the effect of cations. The following chemicals (all from FUJIFILM Wako Pure Chemical Corporation, Japan) were used: cobalt(II) nitrate hexahydrate, nickel(II) nitrate hexahydrate, sodium nitrate, barium nitrate, magnesium nitrate hexahydrate, calcium chloride dihydrate, lithium chloride, iron(III) chloride hexahydrate. The nitrate and chloride salts were prepared into corresponding aqueous solutions (0.05 M in all cases). For the ion-exchange, 1 g of the zeolite powder (HSZ-642NAA) was mixed into 100 g of relevant metal solution. The slurry was heated to and maintain at 70 °C under rotation. Thereafter, the zeolite was recovered through filtration, dried at 80 °C overnight and then calcined at 550 °C for 5 h. Sodium ion-exchange of the MFI zeolite (HSZ-822HOA) was done following the same procedure.

Characterizations: Powder XRD patterns of all zeolites were obtained using a Rigaku Ultima IV diffractometer with CuK α radiation ($\lambda = 1.5406 \text{ \AA}$, $V = 40 \text{ kV}$, $I = 40 \text{ mA}$) at a scanning rate of 4° min^{-1} . Morphologies of the zeolites were observed using a field emission scanning electron microscope (FE-SEM, JSM-7000F, JEOL, Japan). ²⁷Al solid state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) spectra were recorded at 130.33 MHz with a $\pi/2$ pulse length of 3.2 μs , a recycle delay of 5 s, and a spinning frequency of 14 kHz. The pore characteristics were evaluated by nitrogen adsorption-desorption analyses on a Quantachrome Autosorb-iQ2 instrument at liquid nitrogen temperature (77 K). Before the measurements, the samples were pretreated at 325 °C for 4 h under vacuum. Elemental analysis was performed on a Thermo iCAP 6300 inductively coupled plasma-atomic emission spectrometer (ICP-AES).

1. C. T. Chen *et al.*, *Journal of Physical Chemistry C*, 2019, **123**, 20304-20313.

Supporting Table and Figures

Table S1 Chemical compositions of the ion-exchanged zeolites and the natural MOR zeolite

Sample	Si/Al ratio	Na/Al ratio	Me/Al ratio
Na-MOR (HSZ-642NAA)	9.0	1	-
Ca-MOR	9.0	0.13	0.43
Fe-MOR	9.0	0.14	0.79
Ba-MOR	8.4	0.15	0.37
Co-MOR	8.4	0.24	0.34
K-MOR	9.2	-	1
Ni-MOR	8.3	0.22	0.32
Li-MOR	9.0	0.03	0.96
Na-FAU (HSZ-320NAA)	2.8	1	-
Na-MFI	12.0	0.67	-
natural MOR	5.3	0.25	K/Al: 0.11 Ca/Al: 0.20 Fe/Al: 0.08

Note: The chemical compositions were analyzed by ICP-AES. Fluctuation in Si/Al ratio of the ion-exchanged MOR zeolites was probably due to slight dealumination or desilication taking place during the aqueous ion-exchange. For monovalent cations, it was possible to get a fully ion-exchange MOR zeolite (e.g., K-MOR and Li-MOR); whereas for divalent cations, the ion-exchange level could be limited by the number of aluminum pairs in the zeolite, as two neighboring framework charges are needed to balance those divalent cations.

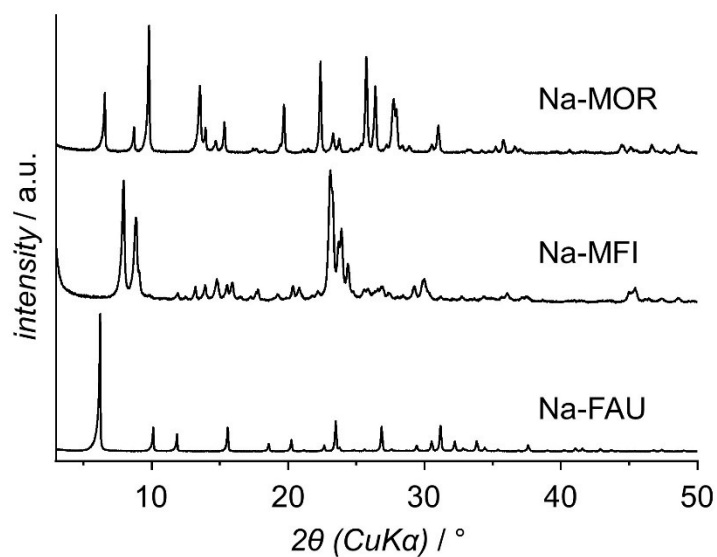


Figure S1. XRD patterns of the sodium-zeolites. (Na-MOR: HSZ-642NAA, Si/Al ratio = 9; Na-FAU: HSZ-320NAA, Si/Al ratio = 2.8; Na-MFI was made by ion-exchange from HSZ-822HOA, which had a Si/Al ratio of 12)

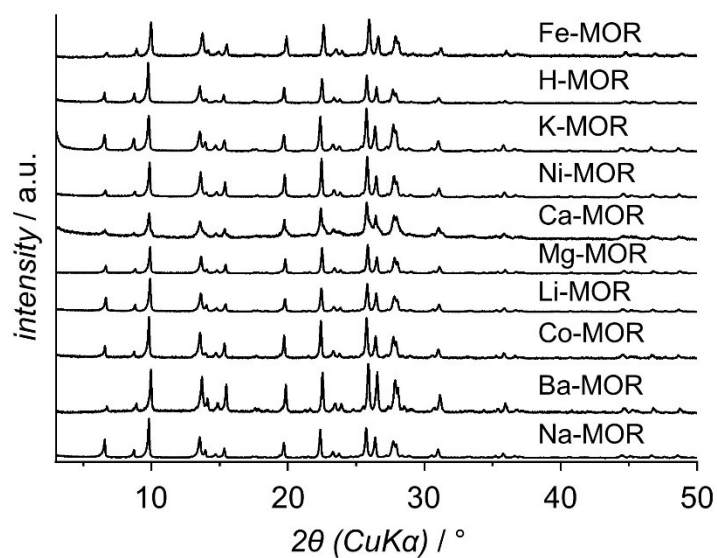


Figure S2. XRD patterns of the MOR zeolites with different types of cation, which were made by ion-exchange from the commercial MOR zeolite with a Si/Al ratio of 9 (HSZ-642NAA).

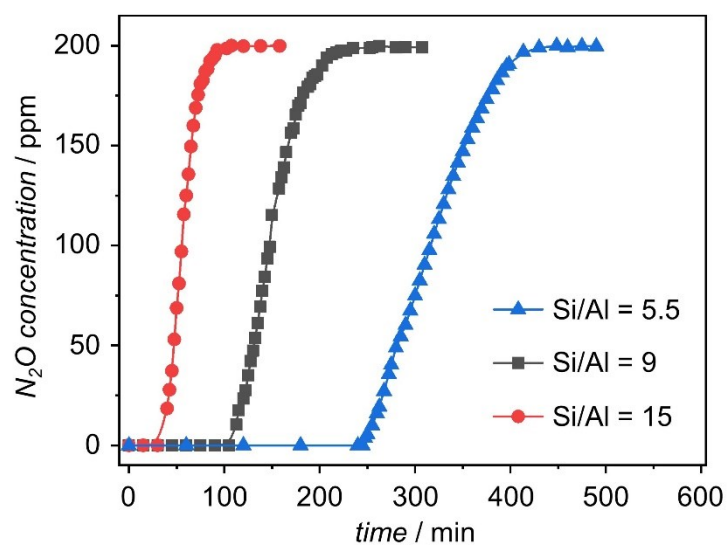


Figure S3. N₂O breakthrough curves for the MOR zeolites with different Si/Al ratios. The breakthrough tests were performed at 25 °C with the N₂O inlet concentration fixed at 200 ppm. The N₂O adsorption capacities for the three zeolites were calculated as follows: 0.04 mmol-N₂O/g-zeolite (Si/Al = 15), 0.17 mmol-N₂O/g-zeolite (Si/Al = 9), and 0.26 mmol-N₂O/g-zeolite (Si/Al = 5.5).

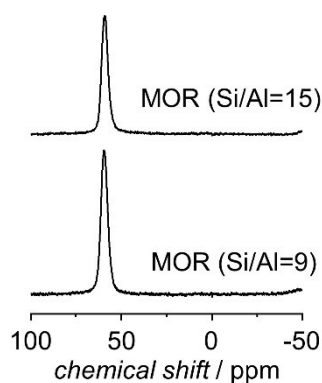


Figure S4. ²⁷Al NMR spectra for the MOR zeolites with different Si/Al ratios.

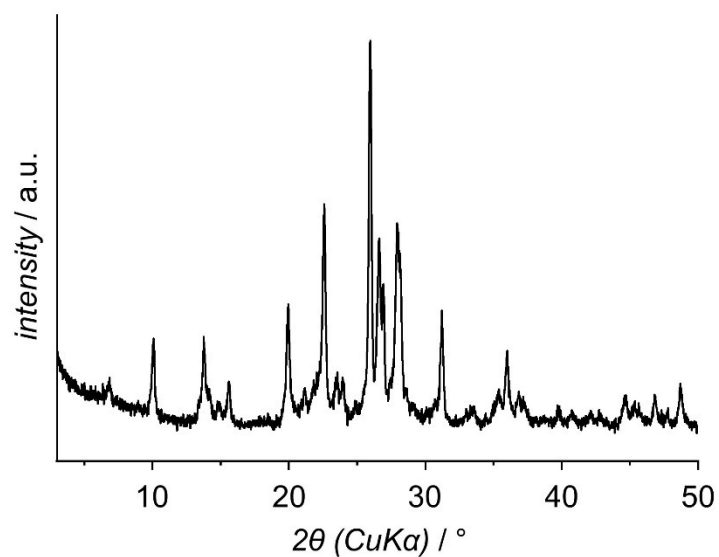


Figure S5. XRD pattern for the natural MOR zeolite.

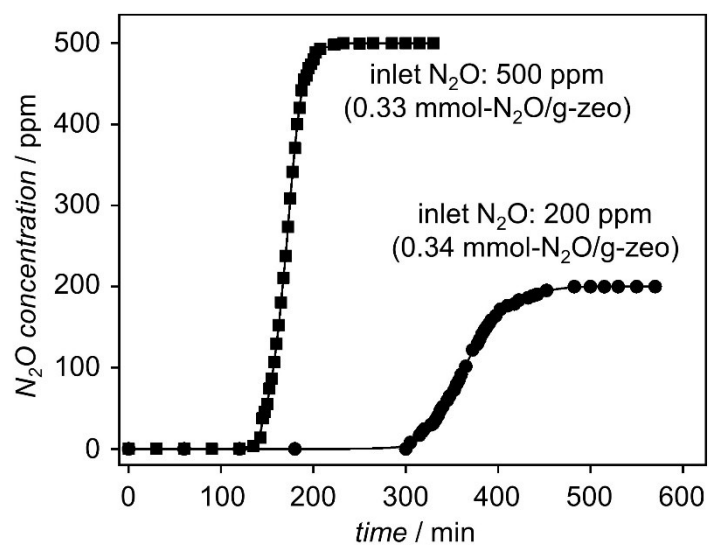


Figure S6. N₂O breakthrough curves for the natural MOR zeolite with different inlet N₂O concentrations. The breakthrough tests were performed at 25 °C.

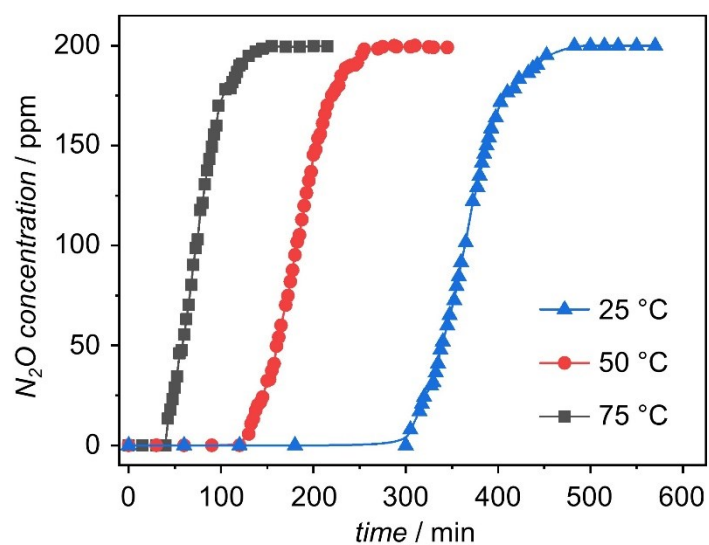


Figure S7. N₂O breakthrough curves for the natural MOR zeolite obtained at different adsorption temperatures with the N₂O inlet concentration fixed at 200 ppm. The N₂O adsorption capacities were calculated as follows: 0.34 mmol-N₂O/g-zeolite (25 °C), 0.21 mmol-N₂O/g-zeolite (50 °C), and 0.06 mmol-N₂O/g-zeolite (75 °C).

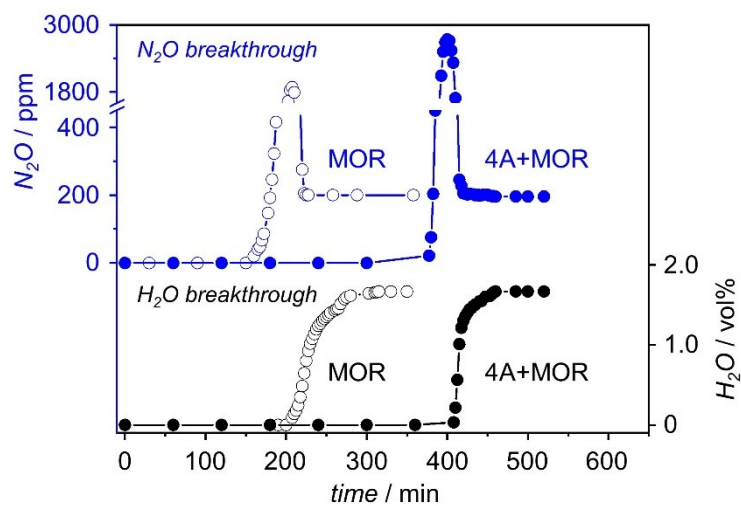


Figure S8. N₂O breakthrough tests in the presence of H₂O. (The feed contained 200 ppm of N₂O and 1.65 vol% of H₂O, and the adsorption temperature was 25 °C. Open circles: only the natural MOR zeolite was used in the breakthrough test. Solid circles: two zeolites were used in the breakthrough test, in which 400 mg of 4A zeolite was placed before the natural MOR zeolite).