

## Supporting Information

### Experimental Section

#### **Materials preparation**

Mordenite zeolites of different Si/Al ratios were obtained from commercial suppliers as follows: CBV21A, Si/Al = 11, in ammonium form was purchased from Zeolyst International. Zeoflair 800, Si/Al = 8.5, in sodium form, and Zeoflair 810, Si/Al = 19, in proton form were obtained from Zeochem. The data presented in the main manuscript for the samples labeled NH<sub>4</sub>-MOR, H-MOR-450, H-MOR-500, MOR-450-NH<sub>4</sub> and MOR-550-NH<sub>4</sub> correspond to modified samples of CBV21A (Si/Al = 11) obtained from Zeolyst International.

#### *Calcination treatment to obtain H-MOR*

The ammonium form of mordenite (CBV21A, Zeolyst International) was calcined in an oven in static air at 450°C or 550°C for 6 h with a heating ramp rate of 1 °C min<sup>-1</sup>. The calcined H-form of mordenite is labelled as H-MOR-450 or alternatively as H-MOR-550, with the number at the end indicating the temperature at which calcination was performed.

#### *Ammonium ion-exchange procedure*

Proton form of the zeolites were converted to the ammonium form by the following procedure: 1 g of zeolite was stirred in 80 mL of 0.1 - 0.5 M solution of ammonium nitrate (> 99%, Sigma-Aldrich) at room temperature overnight with pH monitoring. The suspension was then filtered at room temperature and rinsed with 300 mL of deionized water. This procedure was repeated to obtain the mordenite zeolite in ammonium form. The back-exchanged samples are labelled as MOR-450-NH<sub>4</sub> or alternatively as MOR-550-NH<sub>4</sub>, when the starting proton forms are H-MOR-450 and H-MOR-500 respectively.

#### **Material Characterization**

##### *Solid state <sup>27</sup>Al-MAS-NMR*

<sup>27</sup>Al-MAS-NMR spectra of the zeolites were recorded on a Bruker 400 MHz Ultra-Shield spectrometer. The spectra were accumulated from 3000 scans using a 4 mm probe at a sample spinning rate of 10 kHz. The <sup>27</sup>Al chemical shift was referenced to AlNH<sub>4</sub>(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O at -0.54 ppm and the spectra were acquired using a pulse sequence at a pulse angle of 90 deg and a recovery delay of 1s. The relative amount of aluminum in octahedral coordination was found based on the relative area of the peak centered at 0 ppm.

##### *Solid state <sup>27</sup>Al-MQMAS-NMR*

In an MQ MAS experiment, the quadrupolar interaction is refocused and an isotropic direction, free of anisotropic quadrupolar interactions, can be obtained. The spectra presented herein are such that the F1 axis is the isotropic dimension and the F2 axis contains the second order quadrupolar line shape. <sup>27</sup>Al-MQMAS-NMR spectra of the zeolites were recorded on a Bruker 700 MHz Ultra-Shield spectrometer. The spectra were accumulated from 1440 scans using a 2.5 mm probe at a sample spinning rate of 20 kHz. The spectra were acquired using the mp3qdfs pulse program. In the figures presented in this paper, the <sup>27</sup>Al

MAS NMR spectra are drawn on top of the MQ MAS spectra. These spectra are measured through a separate NMR experiment.

#### *FTIR spectroscopy of carbon monoxide adsorbed over zeolites*

IR spectra were recorded on a Thermo Nicolet iS50 FTIR spectrometer equipped with a DTGS detector at a  $4\text{ cm}^{-1}$  optical resolution and by carrying out 128 scans. Prior to the measurements, the sample (about 20 mg) was pressed in self-supporting discs and activated in the IR transmission cell attached to a vacuum line at 723 K for 4 h. A low temperature vacuum cell cooled with liquid nitrogen was used for carbon monoxide (CO) adsorption measurements. Calibrated aliquots of the gas were introduced into the cell and the spectra were collected immediately. The pressure was measured by a Pfeiffer gauge. Difference spectra were obtained by the subtraction of the spectra of the activated samples from the spectra of the samples with the adsorbate. The presented spectra were normalized to the weight of the samples and compared at similar CO coverage. The subtraction was performed using the OMNIC 9.1 software package.

#### *FTIR spectroscopy of pyridine adsorbed over zeolites*

The activation procedure was the same as the one described above using CO as the probe molecule. For pyridine (Py) adsorption, the samples were exposed to 3 Torr of Py at 423 K for 30 min for the complete diffusion of probe molecules and then, evacuated at the same temperature for 30 min. The peak area analysis was done with OMNIC 9.1 processing software.

#### *Atomic absorption spectroscopy*

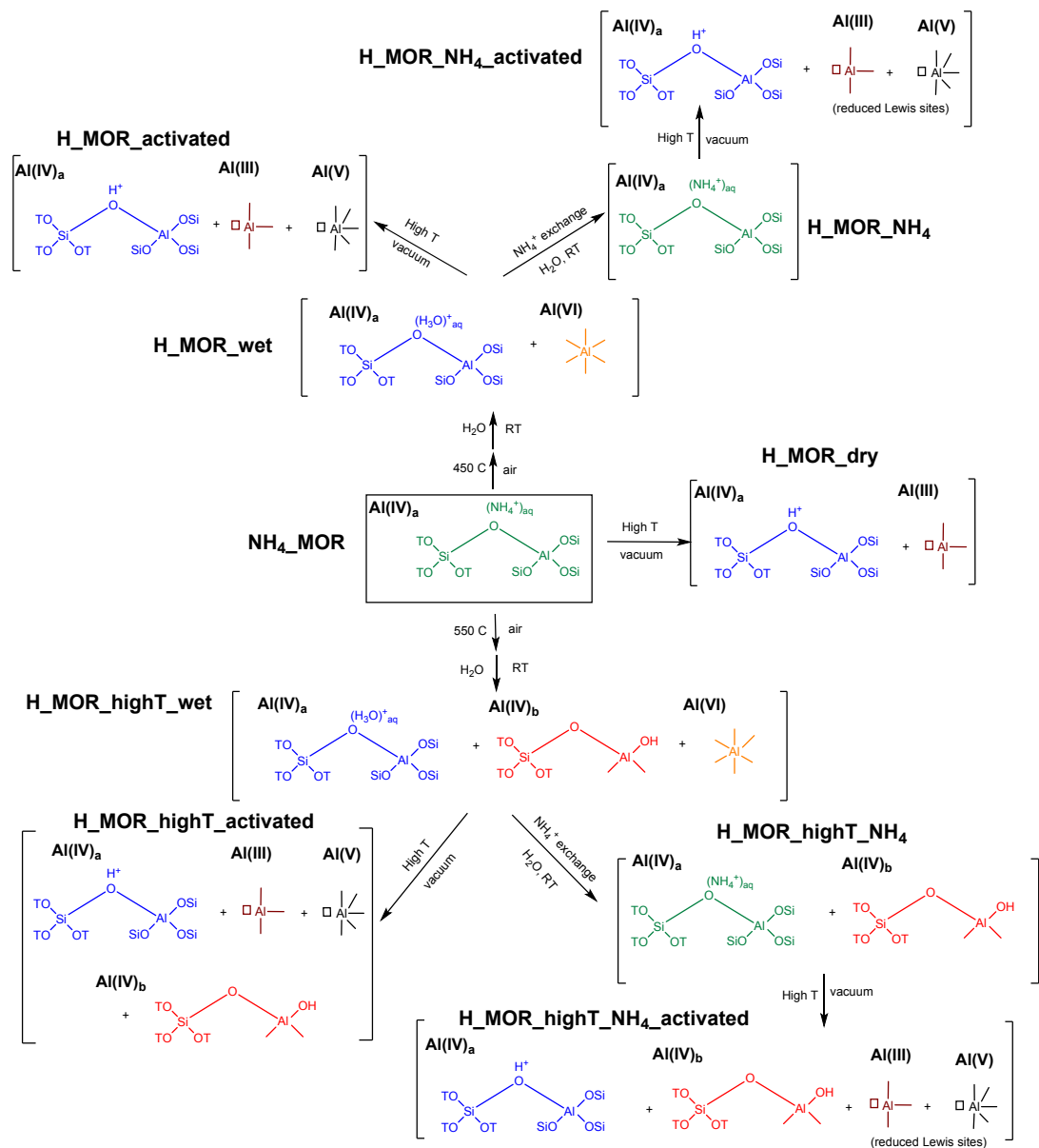
The silicon and aluminum content of various zeolites were determined by AAS. The zeolites (20-50 mg) were dissolved in a mixture of hydrofluoric acid (2-5 mL) and 60% nitric acid (2-5 mL) and diluted with DI-water (25-40 mL). The mixture was stirred at room temperature and diluted to the range of calibration. The resulting solutions were measured with an Agilent SpectrAA 220FS instrument.

**Table S1.** Bulk Si/Al ratio and octahedral aluminum content of zeolite MOR in proton form and after exchanging into ammonium form.

(Si/Al) <sub>bulk</sub> of H-MOR calcined at 550°C <sup>[a]</sup>	% Octahedral aluminum in H-form calcined at 550°C <sup>[b]</sup>	(Si/Al) <sub>bulk</sub> after exchange of H- into NH <sub>4</sub> -form <sup>[a]</sup>	% Octahedral aluminum after exchange of H- into NH <sub>4</sub> -form <sup>[b]</sup>
8.8	13	8.9	0
11.9	11	12.3	0
19.7	10	19.4	0

[a] Determined by AAS; [b] Determined as percentage of corresponding peak area from the <sup>27</sup>Al MAS NMR spectra.

There is no octahedrally-coordinated aluminum in the ammonium-exchanged samples. The Si/Al ratio of the different mordenite samples remains virtually unchanged on ion-exchanging the proton to the ammonium form. This proves the transformation of octahedrally-coordinated aluminum to a tetrahedral coordination on ammonium ion-exchange.



Assignment of species	NMR spectroscopy signature	FTIR spectroscopy signature	Framework Al	Extra-framework Al	Framework-associated Al
Tetrahedral aluminum	Isotropic <sup>27</sup> Al chemical shift at 57 ppm, no anisotropic quadrupolar interaction		✓	✗	N.A.
Distorted tetrahedral aluminum	Isotropic <sup>27</sup> Al chemical shift at 63 ppm, experiences anisotropic quadrupolar interaction	Feature at 3660 cm <sup>-1</sup> corresponding to Al-OH groups	Unlikely	Likely	✗
Bronsted acid sites	Corresponding tetrahedral aluminum has a <sup>27</sup> Al chemical shift at 56 ppm	Feature at 3610 cm <sup>-1</sup> in OH stretching region & upon interaction with pyridine at 1545 cm <sup>-1</sup>	✓	Unlikely	✗
Octahedral aluminum	Isotropic <sup>27</sup> Al chemical shift at 0 ppm		✗	Possible	✓
Lewis acidic three-coordinated aluminum		Feature at 2224 cm <sup>-1</sup> upon interaction with CO	Likely, from framework defects	Maybe	Likely
Lewis acidic five-coordinated aluminum		Feature at 2198 cm <sup>-1</sup> upon interaction with CO	✗	Maybe	Likely

**Scheme S1.** Evolution of aluminum structure in zeolite mordenite with varying conditions as identified by solid-state <sup>27</sup>Al NMR and FTIR spectroscopy of adsorbed pyridine and carbon monoxide.

