Supporting Information for:

Mechanochemically-Assisted Solvent-Free and Template-Free Synthesis of Zeolites ZSM-5 and Mordenite

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Table S1. The solid starting materials for zeolite synthesis using mechanochemical grinding pre-reactions between Na_2SiO_3, $Al_2(SO_4)_3$, and SiO_2 with and without added NaOH.

SiO_2/Al_2O_3 = 30 without NaOH	
Na_2O/Al_2O_3	**Mole ratio of starting materials**
3	26.63 SiO_2 / 2.99 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
4	25.80 SiO_2 / 3.98 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
5	24.13 SiO_2 / 5.03 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
6	23.64 SiO_2 / 5.88 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
7	22.87 SiO_2 / 6.93 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
9	20.64 SiO_2 / 8.80 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$

SiO_2/Al_2O_3 = 30 with NaOH	
Na_2O/Al_2O_3	**Mole ratio of starting materials**
3	27.96 SiO_2 / 1.76 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$/ 2.50 NaOH
4	26.80 SiO_2 / 2.67 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$/ 2.50 NaOH
5	25.97 SiO_2 / 3.69 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$/ 2.50 NaOH
7	23.80 SiO_2 / 5.63 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$/ 2.50 NaOH
9	21.64 SiO_2 / 7.56 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$/ 2.50 NaOH

SiO_2/Al_2O_3 = 40 without NaOH	
Na_2O/Al_2O_3	**Mole ratio of starting materials**
3	36.62 SiO_2 / 3.03 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
4	35.12 SiO_2 / 3.90 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
5	33.95 SiO_2 / 5.02 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
6	33.32 SiO_2 / 5.84 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
7	32.29 SiO_2 / 6.86 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
8	31.62 SiO_2 / 7.88 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$
9	30.96 SiO_2 / 8.83 $Na_2SiO_3 \bullet 9H_2O$/ 0.98 $Al_2(SO_4)_3 \bullet 18H_2O$

SiO_2/Al_2O_3 = 40 with NaOH	
Na_2O/Al_2O_3	**Mole ratio of starting materials**
4	36.28 SiO_2 / 2.74 Na_2SiO_3•$9H_2O$/ 0.98 $Al_2(SO_4)_3$•$18H_2O$/ 2.50 NaOH
5	35.45 SiO_2 / 3.70 Na_2SiO_3•$9H_2O$/ 0.98 $Al_2(SO_4)_3$•$18H_2O$/ 2.50 NaOH
6	34.62 SiO_2 / 4.68 Na_2SiO_3•$9H_2O$/ 0.98 $Al_2(SO_4)_3$•$18H_2O$/ 2.50 NaOH
7	33.29 SiO_2 / 5.74 Na_2SiO_3•$9H_2O$/ 0.98 $Al_2(SO_4)_3$•$18H_2O$/ 2.50 NaOH
8	32.78 SiO_2 / 6.54 Na_2SiO_3•$9H_2O$/ 0.98 $Al_2(SO_4)_3$•$18H_2O$/ 2.50 NaOH
9	31.60 SiO_2 / 7.67 Na_2SiO_3•$9H_2O$/ 0.98 $Al_2(SO_4)_3$•$18H_2O$/ 2.50 NaOH

Table S2. Additional ICP-OES measurements for some of the synthesized samples at different SiO_2/Al_2O_3 and Na_2O/Al_2O_3 ratios using Na_2SiO_3, $Al_2(SO_4)_3$, and SiO_2 reagents with and without NaOH addition.

XRD phase	with NaOH	Equivalent reactant $Na_2O:Al_2O_3:SiO_2$[1]	Product Analysis $Na_2O:Al_2O_3:SiO_2$[2]
amorphous + trace ZSM-5	No	4 : 1 : 30	0.5 : 1 : 18
amorphous + trace ZSM-5	Yes	4 : 1 : 30	0.9 : 1 : 20
amorphous + trace ZSM-5	No	7 : 1 : 40	2.3 : 1: 26
mordenite + trace ZSM-5, quartz	No	9 : 1 : 40	5.3 : 1 : 15

1) Equivalent metal oxide molar ratios are calculated based on the initial moles of the starting materials. Estimates of free sodium after reaction between Na_2SiO_3 and $Al_2(SO_4)_3$ that use 3 molar equivalents Na_2O would result in free sodium and $Na_2O:Al_2O_3$ ratios would be lower by 3 Na_2O (e.g., Na_2O/Al_2O_3 of ratio of 4 becomes 1).

2) The ratios are based on bulk product compositions measured using ICP-OES analysis.

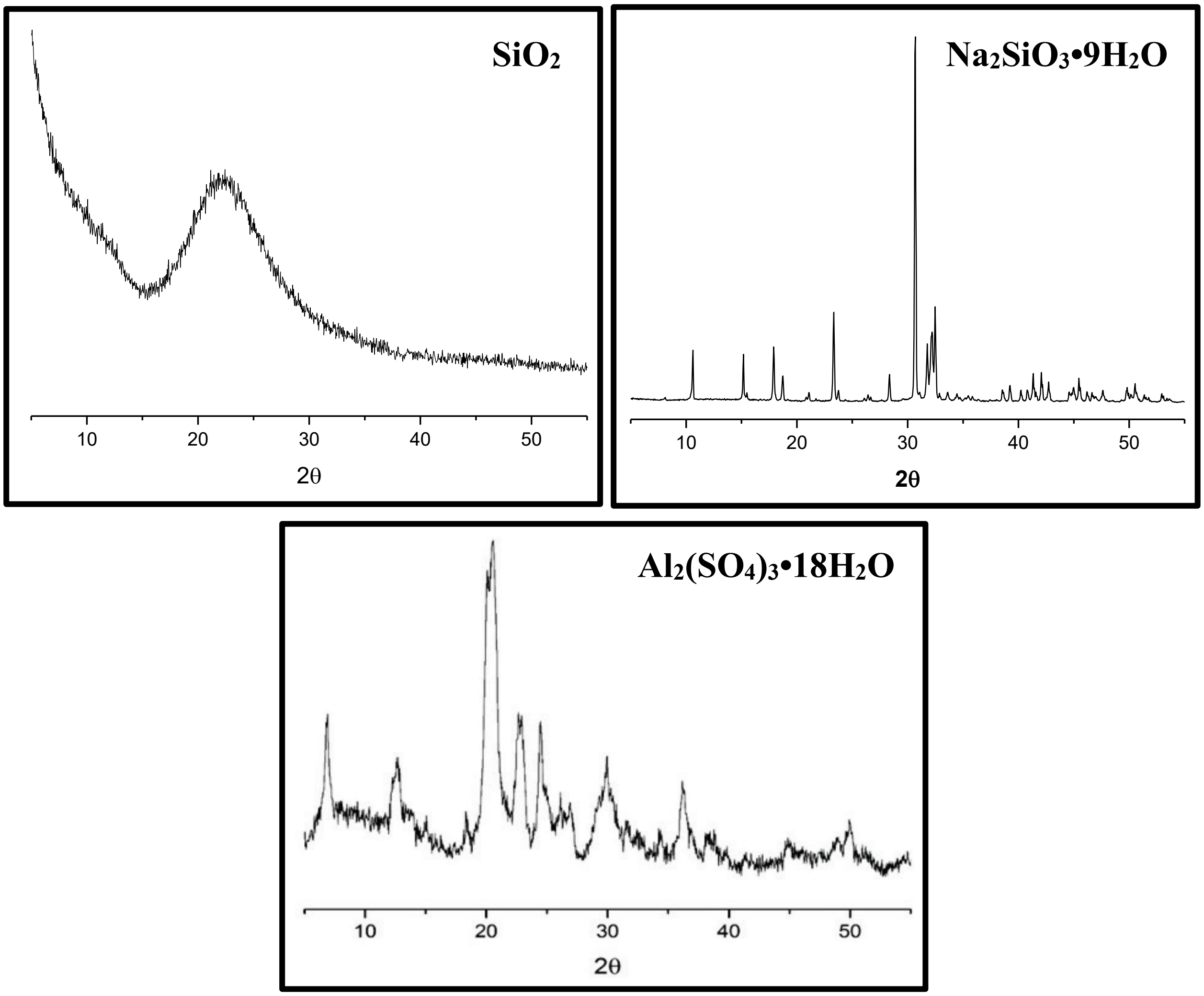

Figure S1. XRD powder patterns of starting materials used in solvent-free, template-free, seed-free zeolite synthesis.

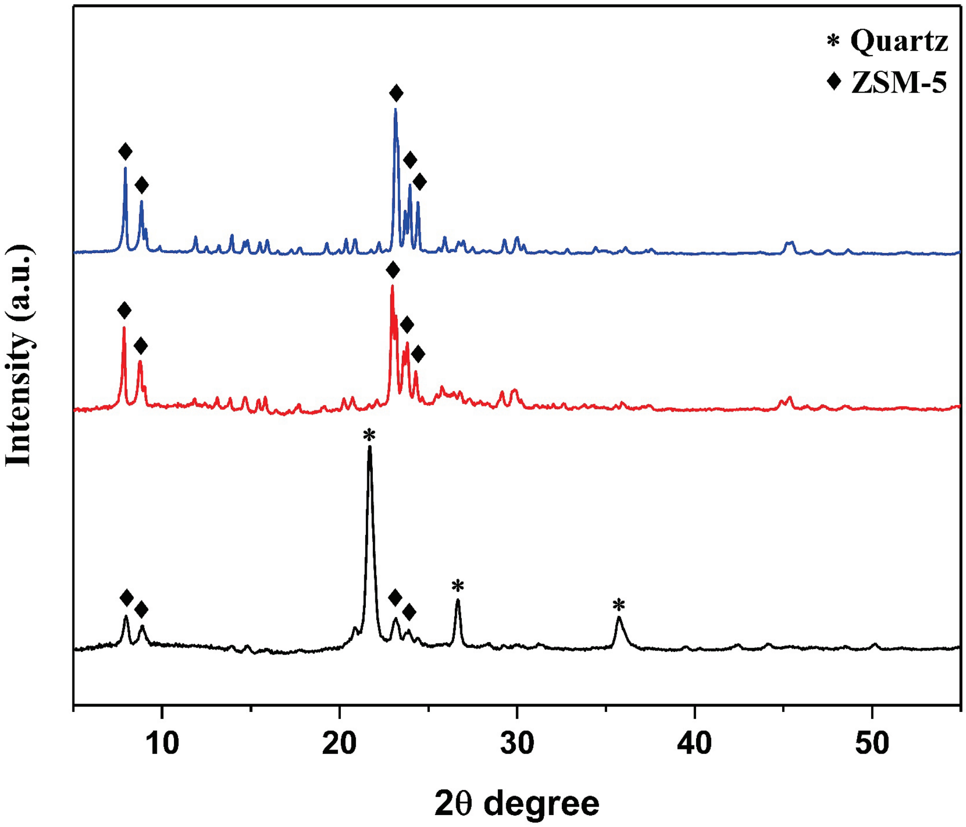

Figure S2. XRD of synthesized ZSM-5 samples after calcination (heating at 550 °C under air). Samples were synthesized with 50 min ball mill grinding at 180 °C for 24 h (black), 48 h (red), and 72 h (blue).

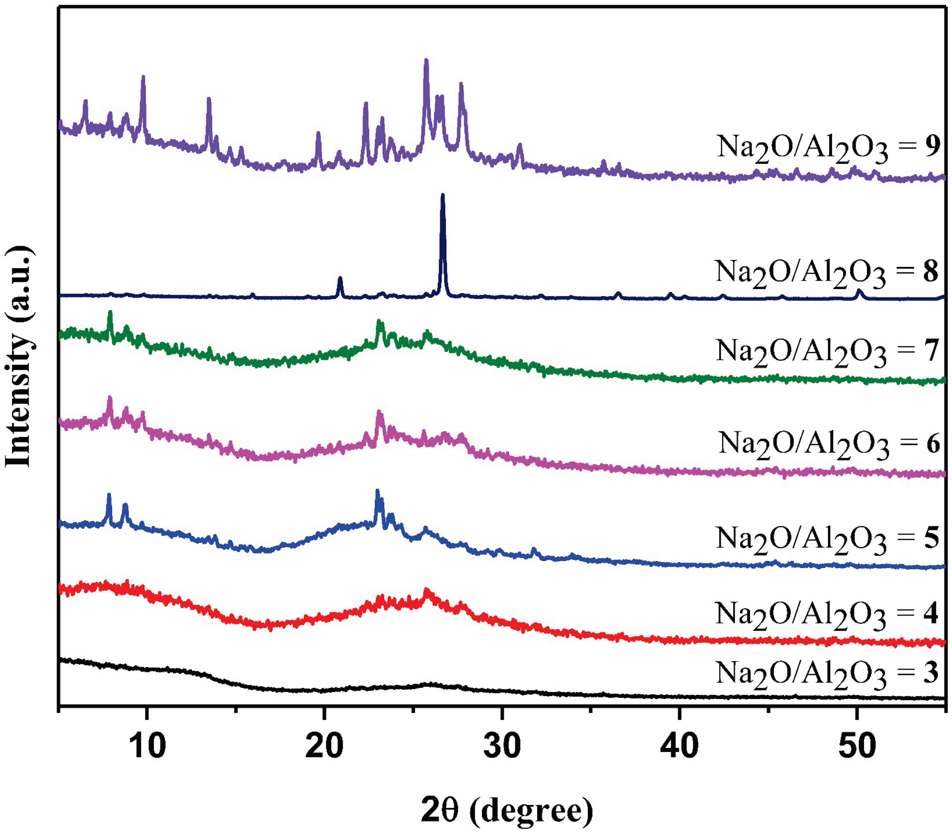

Figure S3. XRD of samples synthesized from a reagent mixture of Na_2SiO_3, $Al_2(SO_4)_3$, and SiO_2 (Na_2O:Al_2O_3:SiO_2 ratio of x:1:40, where x = 3-9) that was mechanochemically ground for 50 min, then thermally treated at 180 °C for 48 h, and then washed with water. Weak peaks for Na_2O/Al_2O_3 of 5-7 correspond to ZSM-5 zeolite, while product for ratio of 8 is dense quartz, and peaks for ratio of 9 are mixed mordenite, ZSM-5, and quartz.

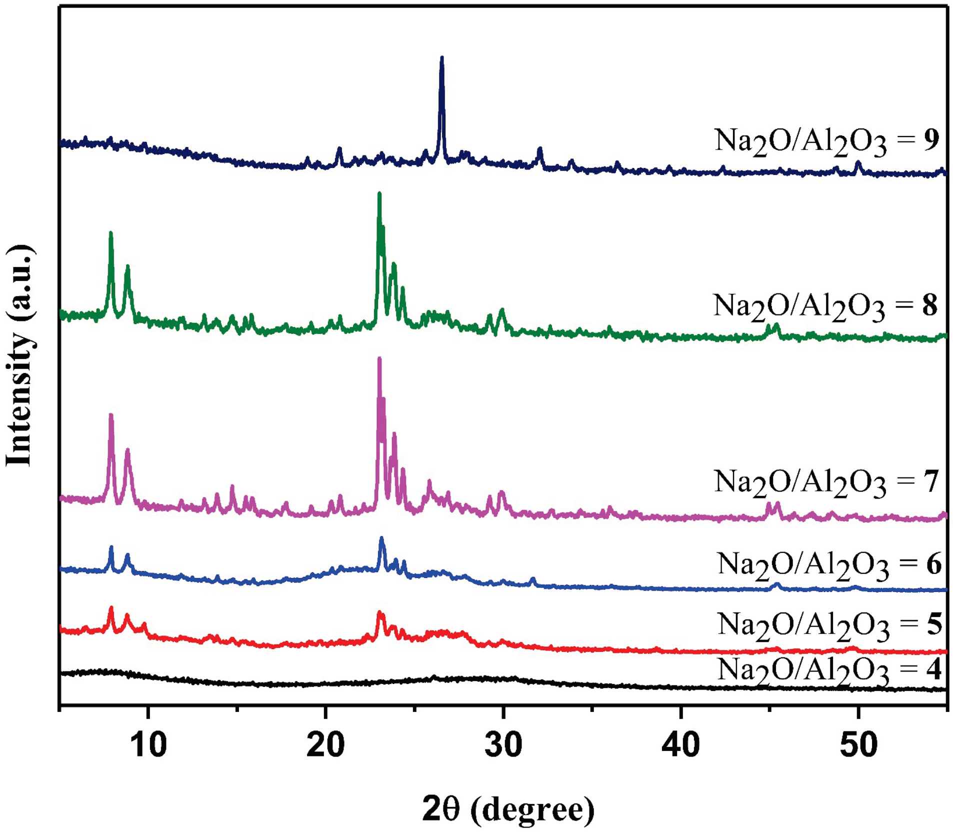

Figure S4. XRD of samples synthesized from a reagent mixture of NaOH, Na_2SiO_3, $Al_2(SO_4)_3$, and SiO_2 (Na_2O:Al_2O_3:SiO_2 ratio of x:1:40, where x = 4-9) that was mechanochemically ground for 50 min, then thermally treated at 180 ºC for 48 h, and then washed with water. The peaks for Na_2O/Al_2O_3 of 5-8 correspond to ZSM-5 zeolite, while product for ratio of 9 is mainly dense quartz.

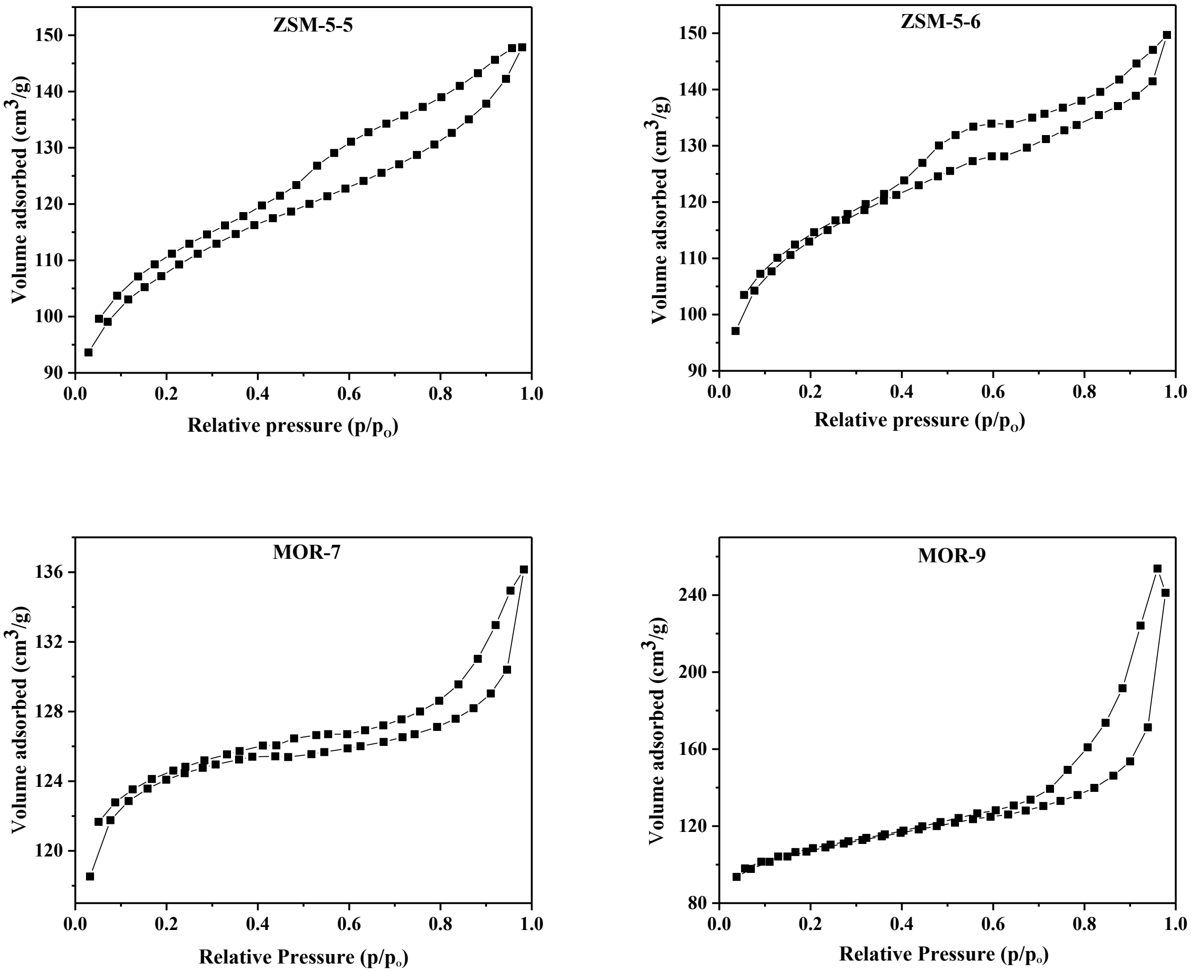

Figure S5. Nitrogen adsorption-desorption isotherm data for as-synthesized ZSM-5-5 sodium form (top left), and acid-exchanged H-ZSM-5-6 (top right) and for as-synthesized MOR-7 sodium form (bottom left) and acid-exchanged H-MOR-9 (bottom right). As-synthesized zeolites were subjected to maximum temperature of 300 °C during BET evacuation and acid-exchanged samples were heated to 550 °C during their synthesis. The seven-point BET surface area results for these samples are shown in Tables 2 and 3.

Pyridine surface reaction studies on acid-exchanged zeolite samples. This analysis was performed based on literature procedures from these references:

Barzetti, T.; Selli, E.; Moscotti, D.; Forni, L. Pyridine and ammonia as probes for FTIR analysis of solid acid catalysts. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1401-1407.

Connerton, J.; Joyner, R. W.; Padley, M. B. Characterisation of the Acidity of Well Defined Cu-ZSM-5 Catalysts using Pyridine as a Probe Molecule. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1841-1844.

Open glass vials with 10 - 15 mg of selected acid-exchanged synthesized and commercial zeolites were placed in a glass reactor that pre-heated to 100 °C. The sample reactor was evacuated at 100 °C for 1 hr then refilled with N_2 gas. Reagent grade pyridine (EM sciences, dried over NaOH pellets) was placed in an Erlenmeyer flask, capped with a rubber septum and degassed with an N_2 purge using a steel needle. A steel canula was used to connect the pyridine flask to the glass reactor with the samples at 100 °C and a flow of pyridine saturated N_2 was transferred into the flask through a septum. A bleed needle in the septum insured that the pyridine atmosphere above the heated zeolite samples contained sufficient available pyridine vapor. The pyridine flow was maintained for 1 hr followed by a N_2 flush and reactor/sample evacuation for 15 minutes at 100 °C to remove weakly bound pyridine. The reactor was cooled to room temperature under evacuation and then transferred into an argon-filled glovebox.

The pyridine exposed zeolites were examined by transmission IR using KBr pellets. A mixture of 1-2 mg of zeolite in 50 mg of KBr was ground to form into pressed pellets. Pellets were typically 20-30 mg in total mass and were formed in the glovebox and protected in sealed plastic bag prior to analysis. A Nicolet Nexus 670 FTIR was used with 64 scans at 2 cm^{-1} resolution. The system was purged with N_2 for at least 5 minutes before taking each spectrum. Comparison spectra for acid-exchanged samples before pyridine exposure were obtained with 64 scans at 2 cm^{-1} resolution under a dry air system purge using pellets prepared under ambient air conditions.

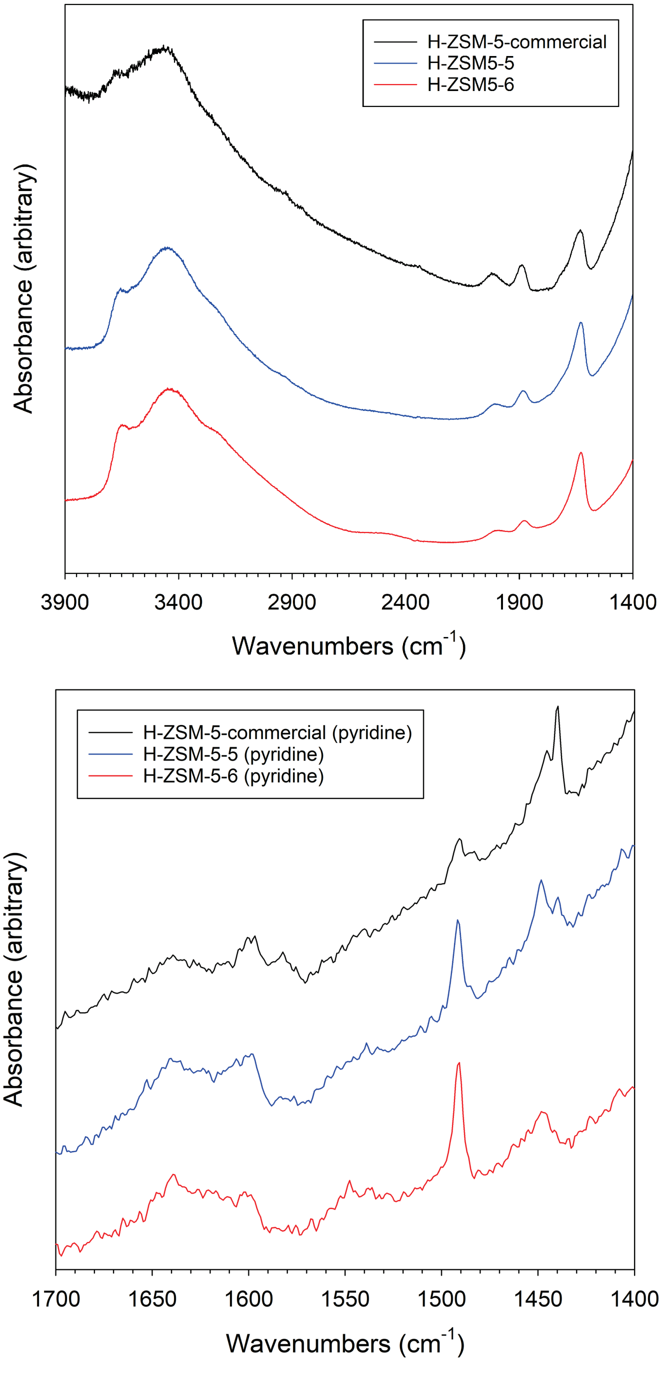

Figure S6. Transmission IR (KBr pellets) comparison of acid-exchanged commercial ZSM-5 with synthesized H-ZSM-5-5 and H-ZSM-5-6 samples before pyridine reaction (top graph) and after pyridine exposure (bottom graph). The major adsorbed water peak in acid-exchanged samples before pyridine exposure is at 1630-1632 cm^{-1}. Pyridine exposed spectra are plotted to highlight the region containing diagnostic peaks for adsorbed pyridine on Lewis acid sites (1621, 1576, 1455 cm^{-1}), molecularly adsorbed pyridine (1599, 1442 cm^{-1}), pyridinium (pyH^{+}, Brønsted sites - 1635, 1545 cm^{-1}), and overlapping pyridine/pyridinium (1490 cm^{-1}) vibrational bands (after Barzetti et. al. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1401 and Connerton et al. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1841).

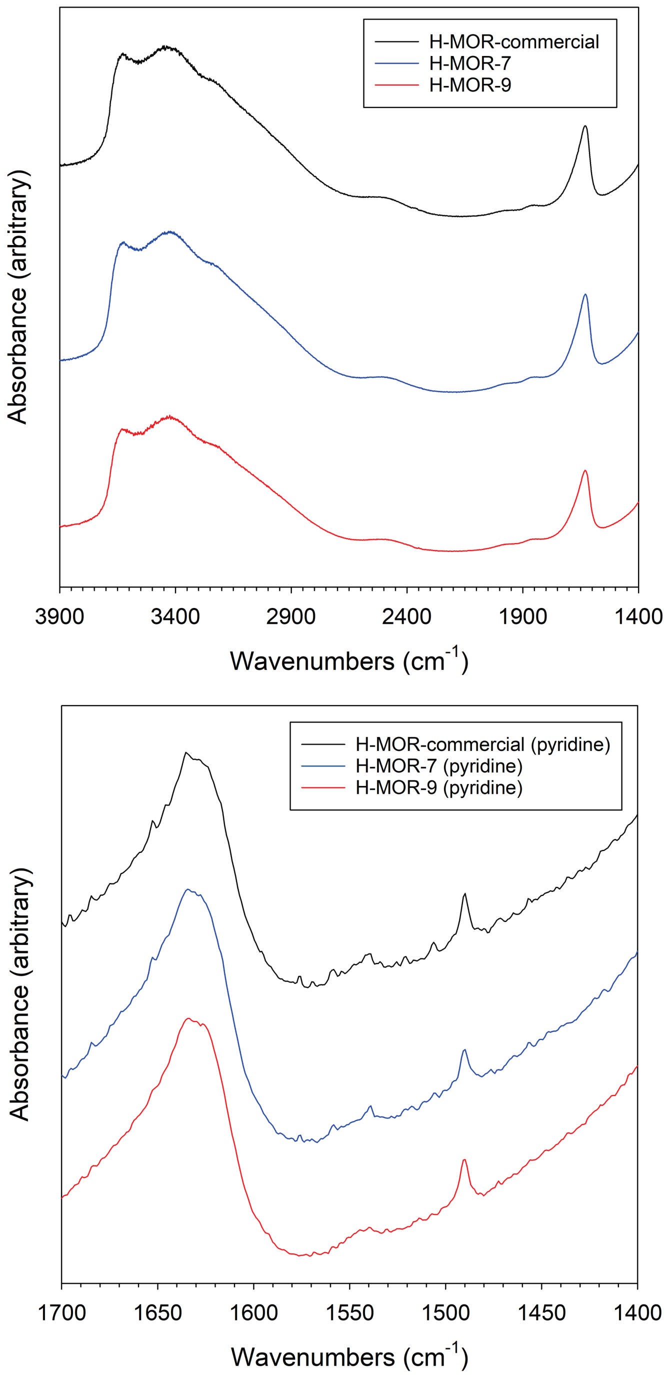

Figure S7. Transmission IR (KBr pellets) comparison of acid-exchanged commercial MOR with synthesized H-MOR-7 and H-MOR-9 samples before pyridine reaction (top graph) and after pyridine exposure (bottom graph). The major adsorbed water peak in acid-exchanged samples before pyridine exposure is at 1630-1632 cm^{-1}. Pyridine exposed spectra are plotted to highlight the region containing diagnostic peaks for adsorbed pyridine on Lewis acid sites (1621, 1576, 1455 cm^{-1}), molecularly adsorbed pyridine (1599, 1442 cm^{-1}), pyridinium (pyH$^+$, Brønsted sites - 1635, 1545 cm^{-1}), and overlapping pyridine/pyridinium (1490 cm^{-1}) vibrational bands (after Barzetti et. al. *J. Chem. Soc., Faraday Trans.* **1996**, *92*, 1401 and Connerton et al. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1841).